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PROCEDURES FOR EVALUATION OF DATA IN ENVIRONMENTAL DATABASES, WITH PARTICULAR REFERENCE TO URANIUM TAILINGS

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PROCEDURES FOR EVALUATION OF DATA IN ENVIRONMENTAL DATABASES, WITH PARTICULAR REFERENCE TO URANIUM TAILINGS

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EXECUTIVE SUMMARY

The increasing use of computer modelling in assessment of environmental impacts calls for compilation of environmental data in a database format suitable for computer retrieval. In the compilation process, much of the supporting documentation relating to the collection and analysis of each sample may be lost. Procedures for evaluating data quality in the absence of such detailed documentation are developed and tested in this report.

Quality-determining characteristics of environmental chemical data sets are discussed, with particular reference to uranium tailings measurements. Specific criteria addressing these characteristics constitute a quality scoring system, with components for analytical methodology, analytical quality control, sampling and sample handling, and continuity of data. Continuity reflects the quantity and distribution of data at a particular site and can be evaluated only in relation to specific project requirements. The other criteria are defined in general terms intended for laboratory rather than individual sample evaluation. Thus, whole blocks of data are scored according to the practices of the laboratories involved in sampling and analysis.

The proposed scoring system is subjective in that it is not based directly on the data to which evaluation scores are applied. Nevertheless, good laboratory and sampling practices may be expected to produce high quality data. It is recommended that subjective evaluation scores should be used only as a first step in selecting data from a set which is larger than required, and should not preclude the use of more objective data quality checks.

Objective data quality checks include such tests as mass balance and anion-cation balance on each sample, and identification of unexplained statistical outliers in a set of samples. From these checks, an 'error rate' or frequency of suspect samples can be derived. In four data sets evaluated during the present study, error rates ranged from less than 1 to 5% and tended to be highest in data sets with the lowest average subjective evaluation scores. However, evaluation scores for these data sets were relatively invariant, ranging from 5 to 8 on a quality scale of 0 (poor) to 9 (good).

Subjective evaluation scores on a simple numeric or alphabetic scale could be incorporated into a database as a guide to users in selection of data. It is recommended that scores for the different components of data quality be listed separately, rather than pooled into a composite score, in order to reflect the strengths and possible weaknesses of each block of data. This recognizes the fact that different users may have different priorities in selecting data, depending on their application.

Documentation in support of subjective evaluation scores should be maintained on file, and updated, with score revision as necessary. This provision allows for changes in laboratory practice and associated changes in expected data quality.

RÉSUMÉ

L'utilisation croissante des ordinateurs dans l'évaluation des impacts environnementaux exige la compilation de données qui soient dans un format facilement accessible par ordinateurs et terminaux. Au cours du processus de compilation, une importante partie de la documentation de support provenant de la collecte et de l'analyse de chaque échantillon est généralement perdue. Des méthodes permettant d'évaluer la qualité des données en l'absence de cette documentation détaillée sont développées et évaluées dans ce rapport.

A l'aide de séries de données chimiques environnementales reliées à des résidus d'uranium, des caractéristiques d'évaluation qualitative sont discutées. Des critères spécifiques représentant ces caractéristiques constituent un système d'attribution de cotes qualitatives dont les composantes représentent la méthodologie analytique, le contrôle de la qualité analytique, la collecte et la manipulation des données et la continuité des données. Celle-ci reflète la quantité et la distribution des données pour un site particulier et ne peut être évaluée qu'en rapport avec les besoins spécifiques d'un projet. Les autres critères se définissent en termes généraux s'appliquant à l'évaluation des laboratoires plutôt qu'à des échantillons individuels. Ainsi, des ensembles de données peuvent être évalués selon les pratiques des laboratoires impliqués dans l'échantillonnage et l'analyse.

Le système d'évaluation proposé est subjectif du fait qu'il ne s'appuie pas directement sur les données auxquelles sont attribuées les cotes. Néanmoins, de bonnes techniques de laboratoire et d'échantillonnage produisent généralement des données de qualité. Il est recommandé que ces cotes d'évaluation ne soient utilisées que de façon préliminaire lors de la sélection de données qui proviennent d'ensembles plus larges que nécessaire et qu'elles n'excluent pas l'utilisation de contrôles de qualité des données plus objectifs.

La vérification objective de la qualité des données comprend des contrôles tels que les bilans anions-cations ou bilans de masse pour chacun des échantillons ainsi que l'identification d'échantillons déviants dans une série d'échantillons et dont la déviance n'est pas expliquée. A partir de ces vérifications, un taux d'erreur ou une fréquence d'échantillons suspects peut être dérivé. Dans quatre séries de données

ayant été évaluées au cours de la présente étude, le taux d'erreur a varié de moins de 1% à 5% et a eu tendance à être plus élevé pour les séries de données ayant des cotes inférieures d'évaluation subjective. Les cotes d'évaluation pour ces séries de données se sont cependant montrées relativement stables variant de 5 à 8 sur une échelle de qualité allant de 0 (pauvre) à 9 (bonne).

Des cotes d'évaluation subjective sur une échelle numérique ou alphabétique pourraient être incorporées dans les banques de données en tant que guide pour les utilisateurs devant faire la sélection de données. Il est aussi recommandé que les cotes pour les différentes composantes relatives à la qualité des données soient inscrites séparément plutôt que regroupées dans une cote composée afin de refléter les forces et faiblesses possibles de chaque ensemble de données. Ceci tient compte du fait que différents utilisateurs peuvent avoir des priorités distinctes dans leur choix de données, selon l'application en vue.

La documentation supportant les cotes d'évaluation subjective devrait être gardée en filière et mise à jour avec une revision des cotes selon les besoins. Cette procédure permettrait de tenir compte des changements dans les pratiques de laboratoire et des modifications résultant sur la qualité anticipée des données.

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ENERGY, MINES AND RESOURCES

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1.0 INTRODUCTION

The National Uranium Tailings Program (NUTP) was formed to conduct research into long-term environmental behaviour of uranium mine tailings. This research will provide the database for development of uranium mine close-out guidelines which may, in future, be used as codes of practice by industry.

Data related to uranium mine tailings have and are being collected by many organizations. The Canadian National Uranium Tailings (CANUT) database was created as a repository for data from the many sources (SYSTEMHOUSE LTD., 1983). Additional data is currently being aquired as part of several NUTP sampling studies, and will be separately maintained.

An integral part of the overall NUTP is the assessment of data quality, in order to permit valid probabilistic modelling of long-term behaviour of radionuclides. The modelling results can then be used to assess the long-term environmental impacts of radionuclide release and the risk potential to man. These results will be incorporated into the overall assessment of management strategies or technologies for close-out of any given tailings site.

IEC BEAK was contracted by the NUTP to develop criteria for quality evaluation of repository data from many sources. Such criteria could be applied to evaluation of any data repository, including the CANUT database.

1.1 Background

Mathematical modelling of the environmental consequences of uranium mine tailings requires data of various forms including:

- o the definition of the geometry, masses and other physical attributes of the system;
- o the definition of loadings (i.e., the rate of discharge of contaminants to surface water, groundwater and the atmosphere);
- o derived parameters to describe model coefficients;

- o data for calibrating and verifying a model's predictions of levels of contaminants in various environmental compartments;
- o methodologies for estimating dose commitment to humans; and
- o probabilistic descriptions:
  - of concentration data in various environmental compartments,
  - of model coefficients, and
  - of loadings.

The validity of a model and the confidence that one places in its predictions are a function of the quality of the data used in its development, and the applicability of the model to the real world situation being modelled.

To understand environmental processes, one desires to differentiate analytical and sampling variability from environmental variability which occurs spatially and/or temporally. But data can be statistically quite noisy. Noise in the data can, for example, cause standard deviations to be larger than the mean. Provided the data fit a normal distribution, this could imply that the mean is not significantly different from zero in a statistical sense. For other processes which are evaluated as the ratio of the two numbers, estimates of their variance may be large if the denominator is a small numerical value with a substantial variance. The ability to assess whether the noise is due to environmental fluctuations or due to analytical and sampling error provides a guide to assessing the quantitative description of the environmental processes under consideration.

Monitoring and regulation require data for several purposes, including:

- o assessing trends;
- o determining background concentrations of contaminants;
- o assessing the degree of impact upon the environment of mining and milling activities; and
- o assessing compliance of mining and milling activities with regulatory objectives and environmental quality standards.

In order for a user to make a judgement as to the applicability of the data in the database to his particular requirement, he must have that data identified as to its

"quality". "Quality" in this context may refer to the following areas of potential concern:

- o purpose for which data were collected,
- o sample collection and handling,
- o laboratory analysis, and
- o data reporting.

The protocol and location of sample collection may effect a large degree of uncertainty in the data. In many instances, sampling protocols are not carefully defined and various individuals may collect samples in a variety of ways. The location from where the sample was obtained may be the most important parameter affecting data quality. Uncertainty may also arise during sample handling and preservation. For example, some samplers filter water samples immediately after collection and then add the necessary preservatives in order to stabilize trace elements in solution, preventing precipitation reactions or adsorption onto the walls of the sample container. Others may preserve the sample directly, without filtration, in order to analyze for 'total' trace elements present. The timing of preservation is particularly important for analysis of radium which exhibits strong adsorption and precipitation reactions.

Another area of uncertainty, and perhaps the one given most attention to date, relates to the actual laboratory analysis. The validity (accuracy and precision) of the data can be evaluated by the type of formal quality assurance program, e.g., use of external verifier and reference standards.

The third area of uncertainty relates to the recording of data and examination for accuracy of results. This examination may involve proofing for typographic errors, checking for correlations between total dissolved solids and conductivity, or carrying out an anion-cation balance.

In order to evaluate the "quality" of the data, complementary information is required for the three areas of potential concern. Based on this information, an overall degree of confidence can be placed on the data.

1.2 Study Objectives

The objectives of the overall study were two-fold and were to be achieved in two phases. They are:

- o to develop criteria for the subjective quality evaluation of NUTP data from various sources (PHASE I); and
- o to verify criteria by application to existing data sets and investigation of relationships to objective quality measures (PHASE II).

1.3 Phase I Study Approach

The Phase I study process consisted of the following steps:

1. elaboration of background information on the development of uranium processing relevant to data evaluation (descriptive characteristics - Section 2.0);

2. identification and elaboration of factors affecting quality of the data, separating naturally occurring variability from variability caused by sampling and analytical procedures (quality determining characteristics - Section 3.0);

3. research of available information on quality determining characteristics relevant to past Canadian laboratory operations providing analytical services to the uranium mining and milling sector (Section 3.1);

4. compilation and evaluation of available information on quality determining characteristics from current Canadian laboratories providing or potentially providing analytical services to the uranium mining and milling sector (Section 3.6);

5. definition of an ideal data set which allows for a fully objective, rationally scientific evaluation (Section 4.1);

6. determination of the actual nature of the data in the database and comparison with the ideal data set (Section 4.2);

7. elaboration of a framework for criteria development and assessment of criteria in terms of meeting the perceived needs of users of the database, i.e., for modelling, monitoring and regulation (Section 4.3);

8. preliminary criteria development (Section 4.4);

1.4 Phase II Study Approach

The Phase II study process consisted of the following steps:

1. peer review and revision of criteria (Section 5.1);
2. verification of criteria by investigation of relationships between criteria scores and error rates in real data sets (Section 5.2);
3. recommendations concerning the utility and application of proposed criteria (Section 6.0).

2.0 DESCRIPTIVE CHARACTERISTICS FOR DATA EVALUATION

It was necessary to understand the sources of uncertainty which may affect the data in order to formulate criteria for data evaluation. These sources of uncertainty had to be reviewed within the context of the development of procedures and technologies used as the uranium mining industry evolved. For example, milling technologies have changed from the initial gravity separation techniques to the various carbonate and acid leach processes now in use. Each of these technologies will have associated with it specific tailings and liquid particulate and gaseous effluent characteristics. Furthermore, major changes have occurred in the methods of tailings placement. The following chronology of uranium processing in Canada provides a framework (descriptive characteristics) for the evaluation of historic data.

2.1 History of Uranium Processing in Canada

The use of radium for the treatment of cancer, after its discovery and isolation in 1898 by Madame Curie, stimulated the worldwide search for uranium, which generates radium as an intermediate element in its decay series. The first commercial sources of radium were Czechoslovakia and the Belgium Congo, with the gravity concentrates processed in Belgium. A smaller source involved carnotite ores of the southwest United States, with processing in Pittsburgh, Pennsylvania.

An initial attempt at the commercial recovery of pitchblende in Canada occurred near the Town of Wilberforce (Bancroft area) in 1932-33. However, even at a value in excess of $80,000 per gram of refined radium, economic recovery was not possible from this pegmatite.

The ongoing search in Canada was rewarded by the discovery of high grade uranium ore on the southeast shore of Great Bear Lake in 1930. The discovery was made by the presence of "cobalt bloom", the bright pink mineral erythrite ($Co_3As_2O_8 \cdot 8H_2O$) on the shoreline, a mineral found with highgrade silver mineralization at Cobalt, Ontario. The development of this orebody at Port Radium, Northwest Territories, about 2,200 km by water or 1,300 km by air from the railhead at Waterways, Alberta, involved concentration of the pitchblende by gravity methods, jigs and tables, or by hand. Because of the remoteness of the location, it was more economical to ship the concentrated pitchblende

to Port Hope, Ontario for radium extraction and refining than to ship the necessary chemicals to Great Bear Lake. This highgrade Canadian ore reduced the price of radium to $25,000 to $30,000 per gram. A by-product of the refining process was uranium oxide which sold for $2.50 per pound U_3O_8 and was used as a pigment and glaze for pottery. Virtually no environmental analyses were carried out during this period. Industry and process analyses related principally to the determination of ionizing radiation through the use of the gold leaf electroscope.

In 1942, when the Manhattan Project was inaugurated to produce uranium for military purposes, the Port Radium mine was reopened, this time to produce uranium. This represented the start of uranium ore processing in Canada. A chronology of the uranium mill operations, including the processes used by the mills from the initial gravity uranium plants to the present, is depicted in Table 2.1.

The immediate objective of the milling process in 1942 was to recover the uranium mineral pitchblende. The available method was to "cob" or pick the larger pieces of pitchblende by hand, crush and grind the remainder, and separate the pitchblende and some other heavy metals, by jigs and tables. The concentrated pitchblende was dried, bagged and shipped to Port Hope for processing.

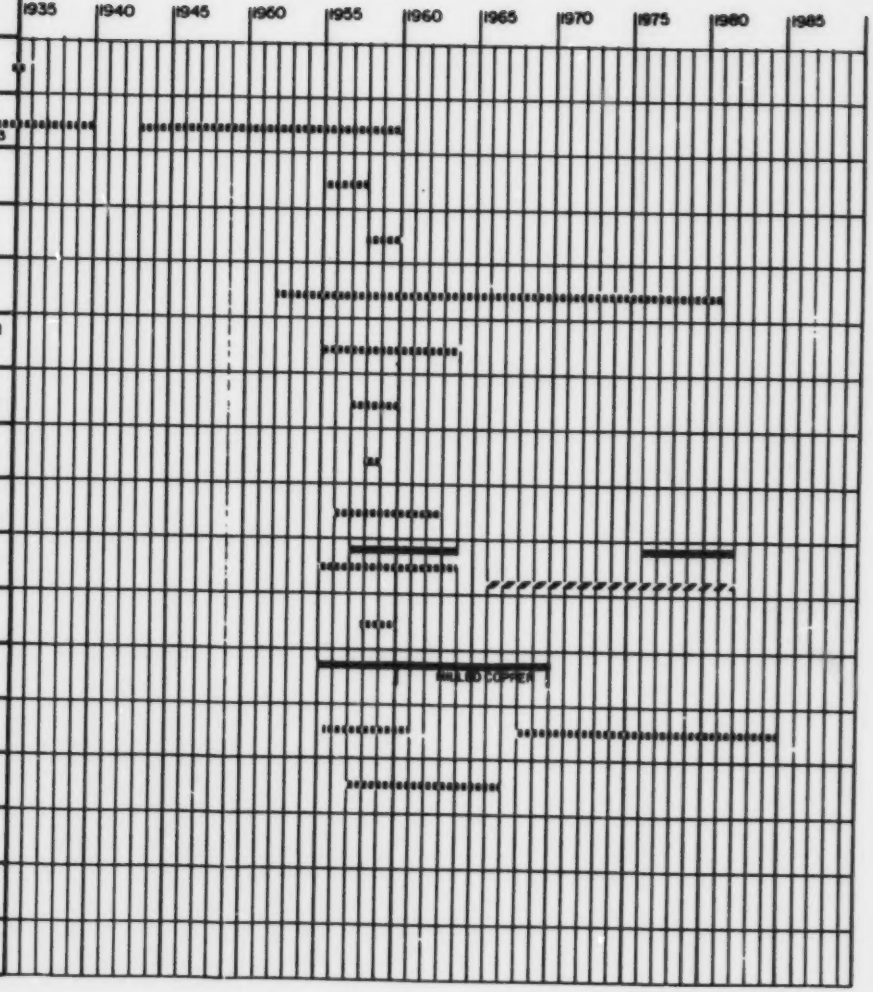
By 1946, it was evident that the high grade ($>1\%$ U_3O_8) ores of Port Radium would run out, and that recovery of uranium from the lower grade ores would require improved methods of recovery. The Mines Branch in Ottawa organized the "Eldorado Project" to investigate the problem. By 1947, it was concluded that gravity methods would not give acceptable recoveries, and hydrometallurgical methods would be required. The Canadian group investigating new methodologies was in close cooperation with similar groups working in the United States, Great Britain and South Africa.

As a result of the research efforts, it was ascertained that uranium could be extracted from the solids and placed in solution with sulphuric acid when certain oxidants were used. The problem of recovery of the uranium from the solution, however, remained, particularly for solutions containing high concentrations of other elements, such as iron, aluminum, arsenic, magnesium, etc.

CANADIAN URANIUM MILLING PLANTS

TABLE 2.1

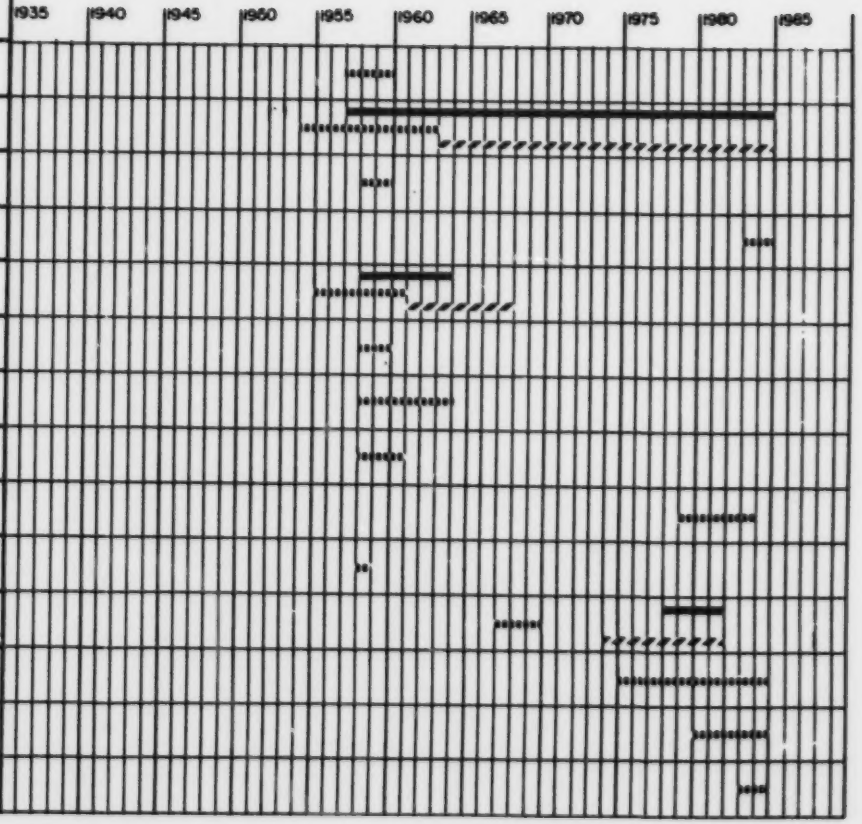
PLANT	ORE TYPE	TYPE OF CIRCUIT	DESIGN CAPACITY (Tonnes/Day)	SOLUTION PURIFICATION	ELUANT / STRIP	PRECIPITANT	TAILING NEUTRALIZATION	MINE WATER
Canadian Radium Wilberforce, Ontario	II	Gravity	<100	--	--	--	Not Req'd	Waste
Eldorado Port Radium, NWT	I	Gravity	100-170	--	--	--	Not Req'd	Waste
Eldorado Port Radium, NWT	I	Acid pH 1.2	170	--	--	As/PO_4	NO	Waste
Eldorado Port Radium, NWT	I	Acid pH 1.2	300	SX	Na_2CO_3	Caustic	NO	Waste
Eldorado * Beaverlodge, Sask.	I	Alkaline (Acid)	750/ 1850	--	--	Caustic	Not Req'd	
Gunnar Beaverlodge, Sask.	I	Acid pH 1.8	1000/ 2000	IX	NaCl	MgO	NO	Untreated
Lorado, Sask.	I	Acid pH 1.8	600	IX	NaCl	MgO	NO	Waste Untreated
Rayrock, NWT	I	Acid pH 1.8	150	IX	NaCl	MgO	NO	Waste Untreated
Bicroft Bancroft, Ontario	II	Acid pH 1.8	1375	IX	NaCl	MgO	YES	Waste Untreated
Madawaska * (Faraday)	II	Acid pH 1.8	1500	IX	NaCl	MgO	YES	Untreated / Treated
Dyno	II	Acid pH 1.8	1100	IX	NaCl	MgO	YES	Untreated
Pronto	III	5% H_2SO_4	1200	IX	NaCl	MgO	YES	Untreated
Quirke	III	5% H_2SO_4	3000	IX	Nitrate	NH_3	YES	Untreated / Treated
Nordic	III	5% H_2SO_4	3700	IX	NO_3	NH_3	YES	Untreated



CANADIAN URANIUM MILLING PLANTS

TABLE 2.I

PLANT	ORE TYPE	TYPE OF CIRCUIT	DESIGN CAPACITY	SOLUTION PURIFICATION	ELUANT STRIP	PRECIPITANT	TAILING NEUTRALIZATION	MINE WATER
Lacnor	III	5% H_2SO_4	4000	IX	HO_3	Caustic	YES	Untreated
Denison	III	5% H_2SO_4	5700/ 15000	IX	NO_3	MgO / NH_3	YES	Untreated to Mill
Stanleigh	III	5% H_2SO_4	5500	IX	NO_3	NH_3	YES	Untreated
Stanleigh	III	5% H_2SO_4	5500	IX	SO_4	MgO	YES	Treated
Stanrock	III	5% H_2SO_4	3300	IX	NO_3	MgO / NH_3	YES	To Waste to Mill
CanMet	III	5% H_2SO_4	3000	IX	NO_3	MgO	YES	Untreated
Milliken	III	5% H_2SO_4	3000	IX	NO_3	NH_3	YES	Untreated
Panel	III	5% H_2SO_4	3000	IX	NO_3	Caustic / MgO	YES	Untreated
Panel	III	5% H_2SO_4	3300	IX	SO_4	MgO	YES	Treated
Spanish	III	5% H_2SO_4	2000	IX	NO_3	Caustic	Yes	Untreated
Agnew Lake *	III	Bacteria pH 1.8		ELUEX	SO_4	NH_3	YES	Untreated / Treated
Gulf Minerals	IV	Acid pH 1.6-1.8	2000	SX	SO_4	NH_3	YES	Treated
Cluff Lake	IV	Gravity/ Acid		SX	SO_4	NH_3	YES	Treated
Key Lake	IV	H_2SO_4	700	SX	SO_4	NH_3	YES	Treated



ORE TYPE	VEIN TYPE (I)	PEGMATITE (II)	REEF (III)	UNCONFORMITY (IV)
URANIUM	0.2-2% U_3O_8 PITCHBLENDE, URANOPHANE, BRANNERITE	0.1-0.2% U_3O_8 URANINITE, URANOTHORITE, THORITE	0.05-0.15% U_3O_8 BRANNERITE, URANOTHORITE, URANINITE	>1% U_3O_8 PITCHBLENDE
SULPHIDES-ARSENIDES	SOME	NONE	3-5% PYRITE-PYRRHOTITE	ARSENIDES-NICKEL SULPHIDES
GANGUE	QUARTZ, CALCITE, SCHIST PHYLLOSILICATES	QUARTZ-FELDSPAR-SYENITE-HORNEBLENDE	QUARTZ PEBBLES, SERICITE MATRIX, BASIC SILICATE WALLROCKS	CLAYS, PHYLLOSILICATES QUARTZ

LEGEND:—
- Period of mill operation
- Period during which mine water untreated
- Period during which mine water discharged to mill.

* decommissioned or decommissioning in progress.

The remote location of Port Radium required the use of sodium chlorate as an oxidant, which had the maximum oxidizing power per unit cost. Uranium precipitation as a mixture of uranous arsenate and phosphate was effected by reducing the separated uranium solution with aluminum powder. Iron remained in solution in the ferrous state. Although analytical chemistry showed significant progress through this period, little or no analysis of an environmental nature was carried out. Most analyses focused on determining ore grades, product recoveries, and grade of product.

In the mid-1950's, two new processes were developed for uranium solution purification:

- ion exchange (IX) using a strong base anion exchanger, and
- solvent extraction (SX) using organophosphorus compounds.

Neither process provided an economic advantage with the Port Radium ore.

In 1954, the Oak Ridge National Laboratory in the United States reported their original research on solvent extraction using amine. This reagent did not require prior reduction of the iron.

In 1958, Port Radium, owned by Eldorado, replaced its recovery system with amine solvent extraction. Sodium diuranate was precipitated with caustic soda. The mine closed in 1960 when the uranium ore reserves were exhausted.

During the 1950's, increased demand for uranium developed in the expanding nuclear power generating industry. Three new uranium fields were developed which came on-stream at about the same time. These were Beaverlodge in Saskatchewan, and the Elliot Lake and Bancroft areas in Ontario. With the exception of the Beaverlodge mine, the new mills employed the sulphuric leach method that was pioneered by the Mines Branch. During this period, sulphuric acid production was generally a by-product of smelter operations. Sulphuric acid transportation to remote locations was uneconomic and, therefore, sulphuric acid had to be produced on-site by Eldorado Port Radium in the Northwest Territories, as well as Gunnar Mines and Lorado Uranium Mines in Saskatchewan. Eldorado and Gunnar used elemental sulphur to make acid. Initially, Lorado floated and roasted the associated pyrite; however, there were insufficient quantities of the sulphide mineral in the ore to produce the necessary tonnage of acid

required. Lorado converted to elemental sulphur when large quantities of this product became available from the sour gas refineries in Alberta. From the inception of uranium milling in Ontario, the excess acid in the tailing slurry was neutralized with lime.

Eldorado Beaverlodge used an alkaline leach primarily, because of the mine's "clean" ore with a high carbonate content. The process involved selective dissolution of uranium as the soluble uranyl tricarbonate anion $UO_2(CO_3)_3^{-4}$, followed by precipitation as sodium diuranate with caustic soda. Acid leaching of a pyrite concentrate was also used to a limited extent.

At the height of uranium demand in the 1950's, there were three mills in the Beaverlodge area of Saskatchewan, two in the Northwest Territories, three in the Bancroft area and eleven in Elliot Lake in Ontario. With the decision of the United States and Great Britain not to renew their contracts in 1960, many of the milling operations were of short duration (Table 2.1). Again, during this phase of development in the industry, environmental concerns were not present, and little data of significance to the NUTP program may be expected.

In 1962, Tsivoglu and O'Connell (1962) of the Robert A. Taft Sanitary Engineering Center in Cleveland, Ohio published a "Waste Guide for the Uranium Milling Industry", following their research on radium-226 in the Animus River. Subsequently, environmental concern was raised in Ontario regarding the increasing levels of dissolved radium in the Serpent River basin and lakes in the Bancroft area. On 13 November 1964, the Ontario Government established a committee of Deputy Ministers to assess the problem, and their report was issued a year later on 24 November 1965. This assessment led to conservation of water in the mills, use of barium chloride to precipitate radium from effluent waters as a barium/radium sulphate sludge, and an increase in the collection of environmentally related data.

The diminution in uranium production continued until the mid-1970's when two new mines, Agnew Lake, near Espanola in Ontario and Gulf Minerals in northeastern Saskatchewan, came on-stream. Both mines incorporated tailings neutralization and radium control.

Agnew Lake developed a bacterially-assisted ferric leach system to extract uranium from the -8" (<20 cm) run of mine ore left underground in the stopes. In addition, the

excess ore or "swell" was heap leached. The "tailings" from this mill consisted of gypsum and precipitated metal hydroxides. In addition, the leached ore required consideration as 'waste rock' which was mixed with tailings and buried on decommissioning.

On 22 September 1976, the Ontario Government passed an Order-In-Council authorizing a hearing by the Environment Assessment Board "into all matters, other than occupational health, relating to the expansion of the uranium mines in the Elliot Lake area". The Board's report was issued in May 1979. Subsequently, on 1 February 1977, the Saskatchewan Government by Order-In-Council appointed three commissioners "to conduct a public inquiry into the probable environmental, health, safety, social, and economic effects of the proposed uranium mine and mill at Cluff Lake, as well as social, economic and other implications of the expansion of the uranium mining industry in Saskatchewan". Their report was issued 31 May 1978.

Both of these Hearings heard from national and international experts on uranium mining and milling in all its aspects. The reports endorsed the expansion of the uranium mining industry in the two provinces, contingent upon prescribed environmental monitoring requirements.

Since 1980, two high grade uranium mines have come on-stream in northern Saskatchewan: Amok's Cluff Lake mine and Key Lake. Both operations have undergone comprehensive environmental reviews and are under the strict control of the Atomic Energy Control Board and Saskatchewan Environment.

2.2 Ore Body Characteristics

For the purpose of this report, the uranium orebodies of Canada have been classified into four types:

- Type I: Vein Type
- Type II: Pegmatite
- Type III: Reef Type
- Type IV: Unconformity Type

The vein and unconformity type producers are found in northern Saskatchewan and the Northwest Territories. The pegmatite and reef type producers are found in Ontario. Uranium discoveries in Labrador, Nova Scotia and British Columbia have not been brought to production and, therefore, are not considered here.

2.2.1 Type I - Vein Type

The vein type ores vary in their mineralogical composition. The predominant uranium mineral is primary pitchblende or uraninite. Minor brannerite was found at the Eldorado Beaverlodge mill, although major brannerite occurred at one mine (Fey). Secondary uranium minerals were rare. While some veins are high grade, mill feed was close to 1% U_3O_8 at Port Radium and about 0.23% U_3O_8 in the Beaverlodge area.

The vein type ore of Port Radium is a complex mixture of minerals including pitchblende, heavy minerals, native silver, arsenides and sulphides. However, within the zone of mined ore (i.e., in the mill feed), the average percentage of sulphides is low. This is reflected by the low specific gravity of the ore.

Most vein type areas had a low sulphide content and a low specific gravity. The specific gravity of the mill feed at Gunnar, for example, was reported as 2.65, similar to the value for quartz. Due to the low sulphide content, element sulphur was sometimes burned to generate SO_2, and hence H_2SO_4 for the acid leach process. This occurred at Lorado where pyrite recovery from the mill feed was insufficient for sulphuric acid generation.

The gangue minerals consisted of various silicates, calcite and typical altered rocks of the Canadian Shield.

2.2.2 Type II - Pegmatites

The pegmatites of the Bancroft area were among the earliest recorded radioactive showings in Canada, e.g., at the Kraft Mine (1916) in Sherbrooke Township in Lanark County. At the operating mines, uranium mineralization was uraninite, uranothorite and thorite, with minor allanite, uranophane and betafite. Mill feed grade was 0.1 to 0.2% U_3O_8. These pegmatites do not contain sulphides.

The gangue minerals consist of the typical feldspars, quartz, hornblende and other silicates that make up the leucogranites and altered rocks of the Canadian Shield.

2.2.3 Type III - Reef Ores

The reef ores of the Elliot Lake area are similar to the conglomerate gold-uranium ores of the Witwatersrand in South Africa, except that the deposits in Canada do not contain gold in economic quantities. The principal uranium minerals are brannerite, uraninite and uranothorite. Some ores have minor amounts of monazite. Mill feeds contain 0.1 to 0.2% U_3O_8. These ores contain pyrite and pyrrhotite in appreciable quantities (3-5%), and mill feed has a specific gravity of 2.75.

Gangue minerals consist of quartz pebbles in a sericite matrix.

2.2.4 Type IV - Unconformity

These ores located in northern Saskatchewan are high grade with mill heads in the percents U_3O_8. The uranium minerals consist of pitchblende, uraninite and coffinite.

The mineralogy is diverse with metal sulphides, arsenides, etc. being common, but total sulphide content is not high. The specific gravity of Gulf Minerals ore is 2.54, a low value which would not be found in sulphide-rich ores.

Gangue minerals consist of altered silicates, clays in feldspatic gneisses and basement series.

2.3 In-Mill Processes

2.3.1 Gravity Methods

The initial milling practice for uranium ore was a gravity method to process the heavy pitchblende into a concentrate assaying 20 to 60% U_3O_8 for shipment to a refinery where the radium was extracted and the uranium was a by-product. This process used no chemicals except water as a vehicle to transport the solids. The gravity plant at Port Radium was closed in 1960. This process was not as efficient as later chemical

extraction processes and, although it did not produce chemical tailings at the mine site, the grade of 'waste rock' was higher than for subsequent operations. Chemical tailings were produced at the refining stage.

The process was revived in 1980 by Amok Ltd. at their high grade Cluff Lake property in northern Saskatchewan. Because of its high specific gravity, the principal ore mineral, pitchblende, could be concentrated by gravity, but, in this case, the concentrate was leached on-site using sulphuric acid. The uranium was precipitated as ammonium diuranate or "yellowcake". The gravity process waste still contains sufficient uranium for economical recovery, and will later be blended with lower grade ore in a conventional sulphuric acid leach plant, producing one integrated tailings material.

2.3.2 Alkaline or Carbonate Leaching

The carbonate leach process is particularly useful in treating acid-consuming (alkaline) ores. The process is based on the fact that uranium will dissolve as the uranyl tricarbonate anion $UO_2(CO_3)_3^{-4}$ in carbonate solutions. The solution, after separation, is treated with excess caustic to precipitate sodium diuranate.

The carbonate leach process is expensive because a finer grind is required than for acid leaching, and grinding is more difficult due to slippage in alkaline ores. In addition, the process requires precise control over the water balance making plant operations difficult. The oxidized uranium minerals are generally easier to dissolve in carbonate solution than minerals such as brannerite. Overall extraction efficiency is lower when carbonate leaching is employed than for the acid leach process.

The only Canadian mill that has employed this method was Eldorado Beaverlodge which has been decommissioned.

2.3.3 Sulphuric Acid Leaching

The development of the sulphuric acid leach was outlined in Section 2.1. This section will examine the unit processes that make up a sulphuric acid leach, particularly as they affect waste management.

Grinding

The grind in water, prior to sulphuric acid leaching, does not require the fineness of the carbonate leach. Initially, all uranium mills used a two-stage rod mill - ball mill combination to reduce the mill feed to fifty percent -200 mesh. This product is referred to as neutral pulp. Steel consumption was about 1.8 kg/tonne of ground ore. This steel consumed acid and left the mill with the tailings, either as a soluble iron salt from those mills that did not neutralize their tailings, or as ferric hydroxide from those mills that practiced neutralization of their tailings.

Between 1958 and 1960, many mills converted their ball mills to pebble mills using a scalped -6"+2" (i.e., 2" < diameter < 6") ore pebble in place of steel balls. This reduced acid and steel consumption, as well as the amount of iron discharged with the tailing.

Neutral Thickening

The neutral pulp from the grinder is dewatered to increase the density and minimize the amount of acid required to obtain the predetermined concentration. The excess water contained radium-226 as well as some dissolved salts such as ammonium nitrate from blasting operations underground. This contaminated water was initially discharged directly to the tailings as waste.

Since about 1963, this water has been recirculated to the grinding circuit conserving the use of fresh water. Since 1964, mine water has been neutralized and recycled to the neutral thickener, recovering any dissolved uranium and further conserving the amount of fresh water required

Acid Leach

For dissolution to occur in sulphuric acid, uranium must first be in the hexavalent state. To assure this, the electrochemical potential of the solution is increased by oxidizing the ferrous iron to ferric, using sodium chlorate (usually 1 to 2 kg/tonne of ore). The introduction of pebble grinding reduced the excess iron available and, thus, the quantity of sodium chlorate required. The chlorate eventually is discharged with the tailing as chloride. With the introduction of air-agitated pachucas in place of mechanical agitators, some mills found that sodium chlorate was not necessary for oxidation.

The addition of sulphuric acid to the optimum requirement depends on the type of ore. For ore types I, II and IV in which the major uranium minerals are uraninite or pitchblende, a pH of 1.5 to 1.8 is optimum. However, these ores often contain calcite and aluminum silicates. If the acid is added too quickly, the heat of dissolution of sulphuric acid increases the rate of reaction with calcite. This reaction is exothermic, bringing the pulp temperature to the point where the alumina-silicates are also attacked. Such a chain reaction can triple the amount of acid required. To avoid this problem, the acid is added in stages, allowing the heat generated to dissipate, slowing down the ensuing reactions and consequent acid consumption.

Type III ore (Elliot Lake) contains brannerite, a refractory uranium-titanium mineral. To dissolve the uranium, a strong (5%) acid is required at elevated temperatures of 70 to 75°C. To conserve acid, high solid to liquid ratios are used to maintain a high concentration of acid. These conditions destroy iron sulphide minerals such as pyrrhotite and marcasite, but not pyrite, and will attack many silicate minerals. To optimize the recovery of uranium by ion exchange, the sulphate concentrations are reduced by increasing the pH of the pulp (pH 2) by addition of limestone or slaked lime. This precipitates a mixture of calcium sulphate and silicates which may occlude radium in their crystal lattices. These precipitates are discharged with the tailings.

Variations of these procedures have been used. Denison Mines initially used a recycle leach to conserve acid, but the cost of filtering the strong acid solution to obtain the recycle solution offset the saving. Milliken Mine (Elliot Lake) used a two-stage leach to minimize acid consumption. This two-stage leach relied on the natural acid consumption in fresh ore to neutralize the excess acid prior to ion exchange. This theoretically should reduce the gypsum content of the final tailing and possibly increase the soluble silicate content of the initially recycled leach liquor.

At Agnew Lake which contains low grade Type III ore, bacteria were used to oxidize pyrite and other sulphides, to sulphuric acid and ferric iron. At Key Lake Mine with a Type IV ore, a two-stage leach is used incorporating a second stage under pressure to use natural sulphides to produce acid and ferric iron. For both these methods, the final tailings is low in sulphide minerals.

Liquid-Solid Separation

After dissolving the uranium, the next step is to separate the uranium solution from the waste solids (or tailing). This process is carried out either by filtration or counter current decantation (CCD). The CCD process, except for the addition of small amounts of settling agents, such as high molecular weight polyethylenimine, has no effect on the behaviour of radionuclides and trace elements in tailings.

Solution Purification and Uranium Precipitation

Two basic methods of solution purification are used in Canada:

- ion exchange (IX) with low grade solutions, and
- solvent extraction (SX) using a tertiary amine.

As indicated in Table 2.1, Eldorado Port Radium used solvent extraction in 1958. However, ion exchange was the preferred method at all other mines, until Gulf Minerals came on-stream in 1975. The ion exchange process uses a strongly basic quartenary ammonium anion exchange resin that will selectively absorb the uranyl anion.

Three eluting solutions have been used prior to uranium precipitation: acidified sodium chloride, ammonium nitrate, and sulphate as 10% sulphuric acid. Mills treating Type I ore in Beaverlodge used chloride (common salt) for elution and magnesia for precipitation, primarily because of the logistics and cost of transporting chemicals to the mine. Similarly, the mills in the Bancroft area with Type II ore used a chloride elution and magnesia precipitation.

Mills in the Elliot Lake area, with the exception of Pronto, used a nitrate elution and precipitation with ammonia. Because Type III ore solutions contain iron and excess sulphate, precipitation is a two-stage process. First, the pH is increased to 3.5 to precipitate iron and sulphate. Because this step requires careful control, lime is used to neutralize most of the acid, but the final adjustment is made by gaseous ammonia diluted with air. The gypsum-iron cake is filtered and recycled to the leach. Final precipitation is conducted with an ammonia-air mixture to pH 7. The ammonia diuranate (yellowcake) is filtered, dried, packed in drums and shipped to refineries.

The possible health and environmental impacts of nitrate discharges were investigated at the Environmental Assessment Board (EAB) Hearings in 1978. It was generally concluded that in an area such as Elliot Lake, which is low in phosphate, nitrate is not a major factor in nutrient enrichment. Another concern was related to high concentrations of ammonia which is discharged as ammonium nitrate used for blasting underground, and as small bleeds from the purification and precipitation circuits.

To alleviate these concerns, alternate reagents have been considered. Nitrate could be replaced by chloride, or the less efficient sulphate. However, chlorides also are of environmental concern, whereas sulphate produces a low grade eluate. Panel and Stanleigh are using sulphate in their new circuits. Stanleigh is using a new Canadian technology developed by Himsley Engineering which increases the strength of the final eluent. This process could possibly be used to the same advantage with nitrate, and continuing process development may be expected.

Refinery location is a factor that influenced the type of precipitant used. Yellowcake may be shipped for refining to Eldorado as magnesia diuranate. Off-shore refineries are reluctant to accept this form of yellowcake, because of disposal problems with the final magnesium waste.

Solution purification and uranium precipitation were problems at Agnew Lake Mine because their solution was a lower grade with very high concentrations of ferric iron which will coprecipitate with the uranium. Agnew Lake pioneered Himsley technology to produce a sulphate eluate which was further purified by amine solvent extraction. Precipitation was controlled by ammonia. To mitigate potential ammonia contamination of the environment, an ammonia recovery plant was operated using a lime boil. The choice of lime over caustic was made to keep the TDS of the final effluent low, but scaling made the circuit impossible to operate.

The new mills that are currently processing highgrade ore use amine solvent extraction with an ammonia sulphate strip and ammonia precipitation.

2.4 Tailings Management Practices

Uranium tailings management in Canada has been the product of Canadian milling experience as it developed over the past ninety years. Table 2.1 gives the chronology of uranium milling plants in Canada. Table 2.2 lists the mills in the same chronological order and outlines their approach to tailings management.

Radium milling took place in small tonnage mills in an era when gold was the prime metal mined and milled. Gold was concentrated by gravity separation for recovery by amalgamation and/or leached in an alkaline pulp for recovery by cyanidation. Most Canadian gold ores occurred as quartz veins, with only minor sulphides in altered aluminum silicate host rocks, often with some calcite. The process of cyanidation involved the addition of protective alkali used to maintain the cyanide levels required for efficient dissolution. Because of the addition of this protective alkali, acid tailings never occurred as a problem.

Mills treating a hundred tonnes of ore per day usually discharged their tailings directly to a lake or other topographic low (Table 2.2, Type A). This approach to impoundment was typical across Canada, and no obvious environmental consequences were immediately evident.

Initially, all large capacity mills in the mining industry used the same method of impoundment. Low-lying regions, such as swamps, were filled and berms were constructed in the appropriate areas to contain the discharged solids. These berms were generally composed of available material such as waste rock or coarse-grained tailings from which the fines had been removed. The purpose of such dams was to maintain low water-table conditions in the fine grained tailings (slimes) and hence increase structural stability in these deposits. Although these techniques appeared to work well in arid regions of the southwestern United States, the higher rates of precipitation in Ontario resulted in the development of standing water on the tailings surface. In order to increase structural stability, overflow or decant systems were added to tailings dams through which excess water was discharged (Table 2.2, Type B). Although this type of impoundment provided a relatively stable mass, major chemical instabilities became apparent in some situations.

MILL TAILING MANAGEMENT

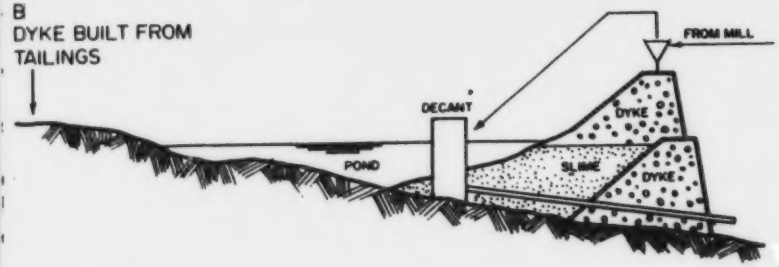
TABLE 2.2

PLANT	MINE WATER	LAKE NEUTRALIZATION	TYPE OF SOLIDS CONTROL	RADIUM CONTROL BARIUM CHLORIDE	MINE BACKFILL
Canadian Radium	Not Treated	Not Req'd	Not Known	NONE	NO
Eldorado Port Radium	Not Treated To 1952	Not Req'd	A	NONE	NO
	1952-1960	NO	A	NONE	
Eldorado Beaverlodge	Not Treated	Not Req'd	A*	After 1971	YES
Gunnar	Not Treated	NO	A and B	NONE	YES
Lorado	Not Treated	NO	A	NONE	NO
Rayrock	Not Treated	NO	A		NO
Bicroft	Not Treated	YES	A and B	NONE	
Faraday	Treated after 1967	YES	A and B	After 1967	YES
Dyno	Not Treated-To Tailing Area	YES	A and B	NONE	NO
Pronto		YES		NONE	
Quirke		YES	A and C	After 1963	
Nordic		YES	A and C		
Lacnor		YES	A		

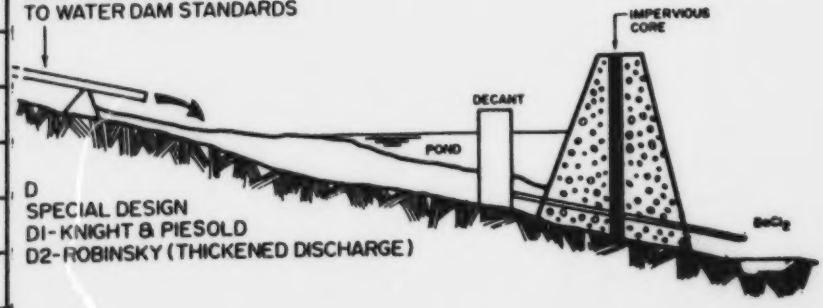
TAILINGS TYPE

A
LAKE DISCHARGE

B
DYKE BUILT FROM TAILINGS



C
IMPERVIOUS DAM BUILT TO WATER DAM STANDARDS



D
SPECIAL DESIGN
D1- KNIGHT & PIESOLD
D2- ROBINSKY (THICKENED DISCHARGE)

MILL TAILING MANAGEMENT

TABLE 2.2

PLANT	MINE WATER	LIME NEUTRAL-IZATION	TYPE OF SOLIDS CONTROL	RADIUM CONTROL BARIUM CHLORIDE	MINE BACKFILL	COMMENTS
Denison	Not Treated to 1964 As Mill Make-up since 1965	YES	D2** A and C	After 1963	NO	
Stanleigh		YES	A and C			
Stanrock	Initially to Waste then to Process, and Mine Solution Processed after Mill Closed	YES	A and B			Stanrock and CanMet shared same tailing area
CanMet	Not Treated	YES	A and B			
Milliken		YES				Two Stage Leach Replaced "Partial Neutralization"
Panel		YES	A and C			
Spanish		YES	A			Tailings with Denison
Agnew Lake	Treated Prior to Operations, Mill Solution During Operations	YES	C	YES	NO	Heap and Stope Leach Technique, Final Waste gypsum and Hydroxide Sludge
Gulf Mineral	Used as Process Water-Excess to Tailing Treatment	YES	C	YES	NO	
Cluff Lake	Process Make-Up	YES	Gravity Tail-in	YES	NO	Small Tonnage of "High Grade Tailing" in Concrete Caskets
Key Lake	Process Make-Up	YES	D1	YES	NO	

* at Beaverlodge lake level did not reach dyke; plan for dyke removal on decommissioning
** D2 solids control under trial at Denison

The Type III uranium ores at Elliot Lake are known to contain significant quantities of iron sulphide mineral (pyrite). When placed in the Type B impoundment, oxidation of this mineral occurs, and the resulting production of sulphuric acid, accompanied by elevated levels of dissolved iron and other species, became evident in the seepage from the toes of tailings dams. These observations were first made in about 1961. It is now known that the acidification process is occurring throughout many tailings deposits in the Elliot Lake region.

Mine water is another component of the mining by-products. The water extracted from the mines is comprised of natural seepage into the excavation, as well as fresh water that is sprayed on the rock faces for dust suppression and is used as an aid to drilling. At Elliot Lake, this water had become acidic and contained elevated concentrations of many metals, including uranium and radium. Prior to 1964, mine waters were discharged directly from the mines to the surface environment, with little or no treatment beyond the settling of solids. As a result of these practices, Quirke Lake into which the effluent was discharged, and the Serpent River system downstream, exhibited decreasing pH values with time. Remedial measures to neutralize the acid mine water were initiated in 1964. In many mines, this neutralized water was substituted for fresh water in the mill, thereby conserving water and recovering the uranium, as well as discharging the precipitated iron and other solids with the mill tailings.

The quantity of mine water for discharge is site-specific. In the case of Eldorado Port Radium mine, seepage was large and, consequently, large volumes of water had to be removed continuously. In contrast, mines at Elliot Lake are generally characterized by very little seepage, with the volume of discharged mine water almost equal to the volume of water brought into the mine for operating purposes. Acidic mine water is also produced under these conditions. Although the treatment of acidic water was implemented soon after its recognition, further concern related to the possible release of radionuclides occurred when studies of the Animus River in the United States were published by the Robert H. Taft Engineering Center in Cincinnati, Ohio in 1962.

The recommendations of the Taft group report included the neutralization of tailings to reduce the discharge of dissolved radium by up to 90%. Standard procedure at uranium mines in Ontario since operations commenced in 1957 was to neutralize tailings before discharge. Initially, surveillance by the Ontario Water Resources Commission of tailings

focused on the control of waste solids. In 1958, however, concern was raised related to the potential contamination of drinking water supplies by radionuclides (e.g., Faraday Mine) and exploratory sampling was initiated. At that time, the concentrations of dissolved radionuclides were not found to be excessive. Systematic monitoring of surface water commenced in 1961 after the Department of Health expanded its radiological laboratory facilities, and the first instance of contamination was noted at Bow Lake in the Bancroft area.

In the Elliot Lake region at that time both mine water and tailings were being treated before discharge, however, it was recognized that remedial action was needed to minimize the impact of acidic contaminated water that was seeping from tailings dams into the surface water regime. It was also known that recycling of the acidic seepage was likely to aggravate the existing situation of pyrite oxidation and acid production. The ferric iron in the seepage effluent would aid further and rapid oxidation of pyrite, and hence intensify the contamination from this source. Because it was thought, at that time, that surface water was the only area of concern, a new type of dam was developed to control seepage from the tailings. This dam, which was designed to be impervious, was modified to contain a clay core (Type C), as well as to provide treatment of the overflow by addition of barium chloride, as well as lime if required. Although this method did not address the subsurface seepage component of water, it provided adequate treatment of the surface water component that was discharged from the tailings impoundment.

To some extent, the design of control measures that would reduce the level of radionuclides in water discharged from mining operations has been hampered by general disagreement among regulatory agencies as to the acceptable levels of radionuclides present in the water. An example of a controversial regulation was that passed by the Congress of the United States in which acceptable treated levels of some radionuclides were expected to be lower than those found in many natural drinking water sources. Some clarification of possible inconsistencies is now probable following the recent recommendation by the ICRP that the maximum acceptable levels of radium be set at 1 Bq/L (27 pCi/L).

Site-specific designs for the disposal of tailings would seem to be the more recent trend (Type D). Dr. Eli Robinsky, at the University of Toronto (Department of Civil

Engineering) introduced the concept of discharging an unsegregated and slightly dewatered "thickened tailings" to impoundments. The resulting deposit would likely be less permeable to water movement as well as less stratified than many of the tailings that were deposited as a slurry. In addition, it is also probable that this material would retain higher water contents even under well-drained conditions, and the consequent decrease in oxygen permeability would result in the reduction of pyrite oxidation and accompanying acid production. This approach is currently being evaluated in the Elliot Lake region, and is presently being used at the Kidd Creek Mine in Timmins, Ontario. Other site-specific designs are being considered as well. One such plan was proposed by Knight and Piesold Ltd. for the Key Lake mine in northern Saskatchewan that includes the deposition of a less permeable mass to reduce subsequent seepage. Another site-specific design is being employed by Eldor Resources at Rabbit Lake where tailings are being placed in a mined-out open pit, surrounded by a permeable crushed rock zone and capped on the surface. The problems of tailings management are currently being examined by the mining companies in an attempt to develop acceptable solutions.

2.5 Tailings Chemistry

The chemistry of uranium tailings can be divided into solid, aqueous and gaseous components. In general, however, the critical aspects of these components are a result of a number of important factors, and are often related to the mining region if not the specific site. The composition of the tailings and its associated water is most strongly affected by the original composition of the ore itself. However, the mining and milling processes and treatment of the discharge, as well as the method of disposal, also affect the resulting chemistry, especially of the aqueous component. Because of the site-specificity of ore composition, and because different mill treatments have been applied, only a generic discussion of tailings chemistry will be given here.

The uranium deposits in Canada can be classified into four distinct types (Table 2.1). Those in the Elliot Lake region of Ontario, for example, are low-grade metamorphosed quartz conglomerates composed mainly of quartz pebbles, but also containing a number of other alumino-silicate minerals in lesser amounts. These deposits also contain up to about 7 percent of sulphide minerals, comprised dominantly of pyrite (FeS_2) and pyrrhotite (Fe_xS_{x+1}). In contrast to these, the deposits of northern Saskatchewan are generally much richer in uranium, and occur in metasedimentary rocks and unconformity

zones. The mineralogy is usually more complex and, in addition to the many silicate minerals associated with the host rock, there are often suites of metal sulphides, arsenides (As) and selenides (Se). Whereas pyrite is not as abundant in these deposits, calcite and other carbonate minerals occur more frequently. Because the uranium deposits differ in their acid-consuming potential (i.e., carbonates or other acid-consumers), two methods had been applied to the milling of these ores. At one mine (Beaverlodge), the alkaline leach process was practiced. However, at all other mines, including those others in Saskatchewan, the sulphuric acid leach process is used.

After extraction of the uranium from the liquid phase, the mill solids and spent process water are then neutralized with limestone ($CaCO_3$) and/or lime (CaO) before discharge to tailings impoundments.

The sulphuric acid leach method produces a highly acidic solution containing large concentrations of sulphate and iron, as well as other metals and radionuclides. Final neutralization before discharge produces solid precipitates (secondary minerals) such as gypsum ($CaSO_4 \cdot 2H_2O$) and ferric hydroxide ($Fe(OH)_3$). Minor quantities of iron and/or aluminum sulphate minerals, such as jarosite ($KFe_3(SO_4)_2(OH)_6$) and jurbanite ($Al(SO_4)(OH) \cdot 5H_2O$) may actually form in the acidic mill water. Some or all of these secondary minerals play a role in the geochemistry of radionuclides such as radium-226. Although these tailings are discharged with effluent having pH values in the range of 8 to 10, leaching of lime and pyrite oxidation has caused the pore water within many tailings deposits to decline to the 1 to 3 range. Associated with this acidic pore water are elevated concentrations of metals such as Fe, Al, Cu, Pb, Co and Zn, and to some extent radionuclides such as Th, U and Pb-210.

It is expected that pyrite will oxidize over long periods, gradually leaching from the surface zones and progressing downward into the tailings mass. As the front of active pyrite oxidation moves downward, it is probable that oxidation will slow as a result of the increasing resistance to oxygen transport with depth and water saturation. Secondary minerals, such as the iron and aluminum sulphates, are expected to be leached or altered (i.e., iron and aluminum oxide formation), and calcite (added as limestone in mill) would be leached much more rapidly than the pyrite. The presence of gypsum would be sustained if the rate of pyrite oxidation was sufficient to produce the required sulphate concentrations. Ferric hydroxides would be relatively stable after the acidic zone

associated with the active oxidation front has passed downward. This iron and the remaining silicate minerals would weather in a manner similar to other natural deposits over extended geologic times. In general, the major concerns associated with these deposits are the movement of contaminated acidic pore water as localized seepage into surrounding surface water, and transport of the pore water into the underlying groundwater system where eventual contact with regional surface water is probable.

Tailings deposits that have little or no pyrite do not develop low pH pore water, and hence are not affected by factors such as high iron and sulphate concentrations that are indicative of acidic environments. However, some of these tailings were derived from high grade uranium ore, and hence form a much larger source of uranium daughter products, such as Th-230, Ra-226 and Pb-210.

Many of these deposits also contain arsenides, selenides and some sulphides, and include metals such as Ni, Co, Zn, Pb and Ag. The chemistry of As and Se is complicated by the potential existence of many species, and the pathways of these elements are not well understood, especially in the groundwater environment. Because of their occurrence in relatively high levels in the tailings, and the probable instability of their respective mineral phases, the potential for contamination of local surface water systems and groundwater exists.

The Beaverlodge ore which contained a significant quantity of acid-consuming minerals was subjected to an alkaline leach process. Some of the process water was recycled in order to achieve the precise water balance control required by the process. After milling and extraction of the uranium, the solids and excess alkaline process water were discharged to tailings impoundments.

From the description of tailings types, it is evident that any data collection program must be suited to the tailings of interest. In the most general terms, these can be classified as:

- Pyritic - acidic
- High Grade - alkaline
- Low Grade - alkaline

In the first, the objective would be to collect data that are relevant to acidic or potentially acidic water. In addition, data describing the potential for neutralization of tailings pore water by the solids would also be important. In the second and third cases, more emphasis in data collection would be placed on the potential contamination of water by trace substances under neutral to high pH conditions. It should be emphasized that this classification is rather gross and is only intended to gain a better focus on the major differences that occur among tailings deposits. Most tailings deposits will require the development of a site-specific plan for data collection.

2.6 Environmental Compartments

The frequency and extent of radionuclide and non-radioactive analyses of environmental compartments related to uranium mine and mill operations resulted directly from the development of concern for potential environmental and human health impacts.

Initially, radiometric analyses were employed to assay ores and calculate the potential for recovery in the gravity separation procedure (e.g., estimation of radium concentration by gold leaf electroscope, and measurement of uranium by various gravimetric, volumetric, colorimetric and fluorimetric methods). Similarly, during the 1950's, analytical work was undertaken primarily to support the development of metallurgical treatment processes. Prior to 1958, environmental surveillance of uranium mill operations by the OWRC focussed on the control of suspended solids in the receiving waters.

With the publication of the "Waste Guide for the Uranium Milling Industry" by Tsivoglou and O'Connell (1962), environmental concern was raised in Ontario regarding the increasing levels of soluble radium in the Serpent River basin, as well as lakes in the Bancroft area. Furthermore, the Ontario Department of Health expanded its radiological laboratory facilities in order to do systematic radiochemical analyses of water quality. From 1962 to 1970, water samples for radiological analyses were collected on a monthly basis by mill personnel from natural streams surrounding their property.

The period of 1970 to the present has been the era of the environmental impact assessment process and environmental hearings, such as the Ontario Environmental Assessment Board Inquiry into expansion of the various mines in the Elliot Lake area and

the Cluff Lake Board of Inquiry. During this period, there was an exponential increase in the frequency of radionuclide and non-radiological monitoring of all environmental compartments associated with uranium mining and milling operations, e.g., water, air, soil, rock, tailings, vegetation and animals.

Table 2.3 presents a chronology of the frequency of data by sample type presently contained within the CANUT database, and is indicative of the recent emphasis on environmental monitoring, with an exponential increase in data generation in the mid and late 1970's.

TABLE 2.3: CHRONOLOGY OF DATA FREQUENCY BY SAMPLE TYPE IN THE CANUT DATABASE

Year	Number of Analyses of Sample Type				
	Surface Water[1]	Ground Water[2]	Tailings Water[3]	Extracted Water[4]	Total
1954	1	-	-	-	1
1956	3	-	-	-	3
1958	3	-	-	-	3
1959	11	-	-	-	11
1963	2	-	-	-	2
1969	1	-	-	-	1
1971	2	-	-	-	2
1972	40	-	-	-	40
1973	22	-	1	-	23
1974	21	-	1	-	22
1975	72	-	20	-	92
1976	168	-	40	-	208
1977	398	59	128	-	585
1978	558	73	147	-	778
1979	712	71	177	-	960
1980	720	64	188	-	972
1981	740	167	226	36	1,169
1982	1,460	178	208	45	1,891

1 Surface Water (sample type code 1100), includes lake (1110), pond (1120), river (1130), stream (1140), swamp/bog/marsh (1150), mine waste water (1160), tailings effluent (1170), domestic/industrial waste water (1180).

2 Ground Water (sample type code 1200), includes mine seepage (1210), well (1240), spring (1250).

3 Tailings Water (sample type code 1400), includes tailings pond water (1410) and tailings pond seepage (1420).

4 Extracted Water (sample type code 1500).

3.0 QUALITY DETERMINING CHARACTERISTICS FOR DATA EVALUATION

Relevant Characteristics of Environmental Data

There are several frameworks which could be used for developing criteria. These include:

- o purpose for which data are (were) gathered;
- o environment represented by the data (e.g., mill, tailings, atmosphere, sediments, soils, surface water, groundwater, aquatic organisms, etc.);
- o uses of the database (e.g., modelling, monitoring, regulatory); and
- o causes of poor quality data.

It was proposed that the initial framework be developed according to "causes of poor quality data". The other "potential frameworks" will influence the criteria to be developed and their alternatives.

It was proposed that the following factors which influence the quality of data could be used in developing criteria:

- o sampling procedures and personnel used for different sample types (e.g., minerological compositions, analyses required);
- o sample treatment used;
- o sample preservation techniques used;
- o sample transportation and storage time;
- o analytical procedures used;
- o data reporting procedures used; and
- o quality assurance program in place for each of the above steps.

However, it was recognized that the usefulness of each factor in criteria development would depend on availability of information which could be associated with particular environmental samples and analyses.

Sources of Information

Reviews of environmental chemical data in the literature reveal that there is frequently no way to judge the validity of reported chemical measurements due to inadequate documentation of sampling, analytical and data handling procedures (Van Loon, 1974). Scrutiny of the reports which have contributed to the CANUT database supports this contention. These reports are listed in Table 3.1.

Ontario Ministry of Environment reports, for example, contain no text, as such. They consist of computer-generated data tables. Sampling dates and approximate locations are clearly identified, and all parameters reported with the correct number of significant figures. Parameter values at or below detection limits, or otherwise suspect, are clearly indicated. However, any additional information must be obtained on request with reference to the sample numbers provided.

The Gulf Minerals reports contain large amounts of environmental data, but do not discuss either analytical methodology or identify the laboratories responsible for chemical analyses. Monenco has been identified by Eldorado, Ottawa (Allan Ashbrook, pers. comm.) as the source of Gulf Minerals data from 1981 and 1982.

The MacLaren Ltd. and Golder Associates reports all identify the analytical laboratories responsible for the environmental data which they present. Methodology is discussed or referenced only with respect to data generated in-house.

In addition to the data extracted from Table 3.1 reports, the CANUT database contains information from other federal and provincial databases (NAQUADAT and ESQUADAT). These data originate from various sources, listed in Table 3.2. The analytical laboratories associated with each of these sources change from year to year, and some no longer exist.

The NAQUADAT database is administered by Environment Canada's Water Quality Branch. Federal personnel have generally been involved in sample collection, and chemical analyses have been conducted by federal laboratories.

TABLE 3.1: REPORTS CONTRIBUTING TO THE CANUT DATABASE

Report	Identification of Analytical Labs	Method Description or Reference
MOE (a)	+	-
MOE (b)	+	-
MOE (c)	+	-
MOE (d)	+	-
MOE (e)	+	-
MOE (f)	+	-
MOE (g)	+	-
MOE (h)	+	-
MOE (i)	+	-
MOE (j)	+	-
MOE (k)	+	-
Gulf Minerals 1981	-	-
Gulf Minerals 1982	-	-
MacLaren 1978	+	+
Golder 1977a	+	+
Golder 1977b	+	+
Golder 1978	+	+
Golder 1979	+	+

TABLE 3.2: LABORATORIES CONTRIBUTING TO NAQUADAT AND ESQUADAT DATABASES

Data Source (Administrator)	Period	Contributor	Analytical Laboratory
NAQUADAT (Water Quality Branch)	1954-68	Water Quality Branch	Public Health Engineering Lab Energy, Mines and Resources
	1968-83	Water Quality Branch	WQB Regional Labs
	1983-84	Water Quality Branch	CCIW Water Quality Lab
ESQUADAT (Saskatchewan Environment)	1972-83	Key Lake	Saskatchewan Research Council
	1983-84	Key Lake	Saskatchewan Research Council Key Lake Lab (most metals)
	1972-81	Eldorado	Eldorado, Beaverlodge
	1981-84	Eldorado	Saskatchewan Research Council
	1972-82	Eldor Resources	Saskatchewan Research Council
	1982-84	Eldor Resources	Monenco
	1972-84	Amok Ltd.	Saskatchewan Research Council

The ESQUADAT database is administered by the Saskatchewan Ministry of Environment. Data from uranium developments are provided to the Saskatchewan Ministry by the mining companies. Samples are collected by mine personnel and analyzed either by commercial laboratories or by mine-operated laboratories. In either case, very little supporting documentation is provided to the Ministry, or entered into the database.

Because the reports contributing to the CANUT database contain inadequate information on analytical methodology and quality control, data quality can only be surmised on the basis of typical performance for the laboratory conducting the analysis. Lab performance is probably best evaluated empirically from the results of interlaboratory comparison studies using carefully prepared standard samples. This approach is illustrated by Hume (1973) for trace metals, Dreesen et al. (1979) for trace metals in uranium mill tailings, and by Smith and Steger (1983) and Smith (1983) for radionuclides.

However, the empirical approach can only reflect current laboratory performance. Evaluation of past performance can be based either on internal consistency of old data sets, or on a knowledge of past analytical, data handling and quality assurance procedures. Information on past and present procedures was solicited by IEC BEAK in a questionnaire distributed to 43 analytical laboratories, listed in Table 3.3.

The questionnaire is appended (Appendix 2). A 77% response rate was obtained. Individual responses are confidential. Current laboratory procedures relevant to data quality are discussed in Sections 3.2 to 3.6.

Most respondants provided adequate information on current laboratory procedures, but few were able to supply historical information. To overcome this historic information gap, a generic chronology of laboratory procedures related to uranium processing was developed, primarily based on information on analytical laboratory practices employed at the Bureau of Mines prepared by Ingles (1984) specifically for this study. This chronology is presented in Section 3.1.

TABLE 3.3: LABORATORIES INCLUDED IN INFORMATION SURVEY

Response Processed	
Amok Ltd.	Acres
Key Lake Mines	Enviroclean (MacLarens)
Chemex (Calgary, Vancouver)	University of Alberta
Lakefield Research	Ontario Ministry of Environment
Monenco	Atomic Energy of Canada
IEC BEAK	Canadian Forestry Service
Barringer-Magenta	Freshwater Institute**
Bondar-Clegg	Radiation Protection Bureau
Saskatchewan Research Council	Dept. of Indian and Northern Affairs
Ontario Research Foundation	Rio Algom
Nova Scotia Research Foundation	
Carleton University	No Response
University of Calgary	
University of Toronto	Eldorado, Ottawa
Ontario Geological Survey	Denison Mines
Radiation Protection Lab**	Monserco Labs
Alberta Environmental Centre	X-ray Labs*
Atomic Energy Control Board	Correlation Labs
Canmet (Elliot Lake, Ottawa)	B.C. Research
Wastewater Technology Centre	University of Waterloo
National Water Research Inst.	Geological Survey of Canada
National Hydrology Research Inst.	EPS, Ottawa
Water Quality Lab	National Research Council*

* Response declined

** Partial response obtained, additions promised.

Shipments of pitchblende concentrate were analyzed chemically. No other elements were analyzed at the mine, except for occasional analyses for silver. No regular samples for analysis were taken outside the mill.

With the need to treat lower grade ores by chemical leaching processes, faster analytical methods were required for uranium and associated impurities in both solids and solutions. In the 1950's, uranium analyses were performed fluorimetrically on low grade samples and by ethyl acetate extraction, and the hydrogen-peroxide colorimetric finish on higher grade samples. Analyses for radium or other radionuclides were not required. About 1960, x-ray fluorescence came into use for the analysis of uranium in mill products, and is used by most operators today.

With the development of environmental concern in the early 1960's regarding radium in drinking water, the Ontario Department of Health undertook some radium analysis of surface water samples from Elliot Lake and the Bancroft areas. Prior to this, no mine did on-site analyses for radium or other radionuclides.

From 1962 to 1970, water samples were taken on a regular (monthly) basis by mill personnel from natural streams surrounding the property. A sample was taken from the same location by rinsing out a "two quart" plastic bottle in the stream, filling the bottle and following instructions for sample analysis. Denison sent their samples to the Ontario Department of Health laboratory, whereas Rio Algom analyzed some of their samples internally.

The following is a chronological synopsis of laboratory analytical practices employed by the Bureau of Mines, prepared specifically for this study by Ingles (1984). This synopsis, although specific for the Bureau of Mines laboratory, reflects, in general, the development of analytical capabilities related to uranium processing in Canada.

3.1.1 Chronological Synopsis of Analytical Practices at the Bureau of Mines Laboratory

Introduction

The Radioactivity Division of the Mines Branch had its origin in 1946 as the "Eldorado Project", with the goal of improving uranium recovery at the Port Radium mine (the only

operating mine in Canada). The specific task was to devise methods for decreasing the amount of uranium lost in the gravity mill tails. Concentrations in the tails ran to 0.26% U_3O_8. Initially, attempts were made to improve the gravity method by using more modern equipment, followed by an extensive program using flotation. By 1947, it was clear that leaching methods were needed to improve recovery, and this method predominated thereafter.

Chronology of Radioanalytical Methods

Until 1949, the reliability of available analytical methods for uranium was insufficient to provide the information required. Radiometric methods were used extensively, but could not be used for chemically-altered material, such as solutions and leach tails. Methods for thorium were also being improved over this period. They were not required or used for process investigations until the first investigations on the Bancroft area ores were undertaken in 1955, but were employed on a number of prospector's samples between 1952 and 1954.

These samples contained mostly niobium-tantalum-titanium-uranium minerals that were not amenable to treatment, and the properties never developed into mines. The analytical separations employed varied, depending on the sample type, and this is well illustrated in Method Th-1 of the "Manual for the Uranium Concentrating Plant" (Ingles, 1959).

The Mines Branch laboratory did not become involved in radium analyses until 1958 and then only for water analyses, as the Faraday Mine was encountering radium in drinking water obtained from nearby weils. No further determinations were done until 1974 when a method was set up to provide support for projects on new leach processes aimed at eliminating radium from acid leach tails (Zimmerman and Armstrong, 1975).

Table 3.4 summarizes the chronology of radioanalytical methods used at CANMET and SRC for determination of uranium and thorium series radionuclides. Details are provided in Appendix 1. Brief comments on the methods and their relative merits are discussed in Section 3.3 below.

TABLE 3.4: CHRONOLOGY OF RADIOANALYTICAL METHODS

Method (CANMET)	Time Period (year) 1945 50 55 60 65 70 75 80	Detection Limit	Precision at Concentration*	References
Uranium				
As Volatization H_2 Separation Gravimetric Finish	——	2%	±5% at 5%	Rodden, Furman (1946)
Hg Cathode Separation Volumetric Finish	——	1%	±0.5% at 5%	Rodden, Tregoning (1950)
Cellulose Column Volumetric Finish	——	1%	±0.5% at 5%	Burstall, Williams (1950)
Cellulose Column Colorimetric Finish	——	.001%	±0.5% at 0.1%	Rabbits (1949, 1952)
Ethyl Acetate Separation Colorimetric Finish	————	5%	±0.25% at 5%	Ingles (1959)
Fluorimetric MIT Model 3	————	.00025%	±1.5% at 0.5%	Ingles (1959)
Tributyl Phosphate Separation Colorimetric Finish	————	.005%	±0.005% at 2.5%	Ingles (1959)
Tri-n-octyl Phosphoric Oxide Extraction Bromo PADAP Finish	————	.005%	±1% at 0.005%	Ashbrook (1971)
X-Ray Emission	———— - - -			Zimmerman, Reynolds (1974)

TABLE 3.4: CHRONOLOGY OF RADIOANALYTICAL METHODS

Method (CANMET)	Time Period (year) 1945 50 55 60 65 70 75 80	Detection Limit	Precision at Concentration*	References
Thorium				
Hg Cathode-K Iodate Oxalate Precipitation Gravimetric Finish	——	2%	±10%	Rabbits (1947)
Oxalate-Hexamine Separation Oxalate Precipitation Gravimetric Finish	——	2%	±10%	Rodden, Furman (1946)
Cellulose-Ether Column Oxalate Separation Gravimetric Finish	——	0.005%	±10%	Hunt et al. (1950)
CH_3 Oxalate Separation Mesityl Oxide Extraction Colorimetric Finish	————	0.001%	±5-10%	Ingles (1951, 1959)
Sebacic Acid Separation Mesityl Oxide Extraction Colorimetric Finish	————	0.001%	±5-10%	Ingles (1959)
Radiometric Emanation	————	0.01%	±5-10%	Ingles (1959)
Cation Exchange in HCl Sulphuric Elution Colorimetric Finish	————	0.001%	±5-10%	Ingles et al. (1977)
Thorium-230 Spectrometry	——	5 pCi/g	10%	CANMET (1978-22)

TABLE 3.4: CHRONOLOGY OF RADIOANALYTICAL METHODS

Method (CANMET)	Time Period (year) 1945	50	55	60	65	70	75	80	Detection Limit	Precision at Concentration*	References
Radium											
$BaSO_4$ Co-precipitation Pb Removal Spectrometry							——			±12% at 5 pCi	Zimmerman, Armstrong (1975)
Radium-226											
Spectrometry								——	5 pCi/g	±10% at 5 pCi	CANMET (1978-22)
Spectrometry								——	5 pCi/g	±5% at 10 pCi	CANMET (1978-22) (modified)
Radon Emanation								—			

TABLE 3.4: CHRONOLOGY OF RADIOANALYTICAL METHODS

Method (SRC)	Time Period (year) 1945 50 55 60 65 70 75 80	Detection Limit	Precision at Concentration*	References
Uranium				
UV Fluorescence	———————			Price et al. (1953)
Colorimetric Bromo PADAP Finish	———	0.1 ug	±2%	Johnson, Florence (1971)
Delayed Neutron Counting (Slowpoke II)	——	0.1 ug	±2%	
Neutron Activation Analysis (in-house)	——			
Thorium				
Colorimetric Arsenazo III	———	0.2 ug	±5%	CANMET (1978-22)
Neutron Activation Analysis (in-house)	——	0.05 ug	±3%	
Thorium Isotopes				
Isolation-Electrodeposition Spectrometry	———	0.2 pCi	±8%	CANMET (1978-22)
Isolation-Ce $(OH)_3$ Precipitation Spectrometry	——	0.2 pCi	±8%	Sill, Williams (1981)

TABLE 3.4: CHRONOLOGY OF RADIOANALYTICAL METHODS

Method (SRC)	Time Period (year) 1945 50 55 60 65 70 75 80	Detection Limit	Precision at Concentration*	References
Radium-226				
$BaCO_4$ Precipitation Spectrometry	———	0.1 pCi	±8%	CANMET (1978-22)
Radon Emanation	———	0.1 pCi	±8%	CANMET (1978-22)
Radium-228				
Isolation-Ac-228 Separation Spectrometry	———	1.0 pCi	±6%	CANMET (1978-22)
Radon-222				
Zn Coated Lucas Cell Bare Photo-multiplier	———	0.2 pCi	±10%	
Polonium-210				
Self-deposition on Ag Spectrometry	———	0.1 pCi	±6%	CANMET (1978-22)

* Precision as relative standard deviation (i.e., standard deviation/mean concentration).
-- Indicates supplementary or occasional use of method.

Chronology of Analytical Methods for Heavy Metals

As for non-radioactive elements, methods for arsenic, cobalt, calcium, iron, manganese, nickel, phosphorus and aluminum suitable for use on uranium ores were all established, tested and operating in 1950 (Robson, 1950). Except for nickel, the methods of determination for each of these included a colorimetric and a volumetric version. Adequate sensitivity for most purposes could be achieved.

By 1958, the arsenic method had been modified to make it more sensitive and specific (by combining the distillation separation and the colorimetric finish). Two methods for carbonate were adopted, acid evolution and combustion. A rapid, sensitive colorimetric method for copper was added, as well as a more sensitive colorimetric method for iron (1953). Colorimetric methods were being used for both the nitrate and ammonia forms of nitrogen. A classical gravimetric pyrophosphate method was being used for magnesium determinations. For fluoride, the Willard and Winter distillation separation and a volumetric finish by titration with thorium was employed. Cadmium and chromium determinations were never required in connection with any of the test work on the radioactive ores, nor was there ever any indication of their presence.

The laboratory was equipped with a polarograph from 1949 onward, and the instrumentation was regularly updated to state-of-the-art. A continuing program of method development was maintained, but polarographic methods were seldom used routinely for the radioactive ores program. However, from about 1954 on, lead, copper and zinc, as well as nickel and cobalt, were determined polarographically in connection with other programs. By the early 1970's, the electroanalytical instrumentation permitted the use of a wide variety of techniques, including amperometry, coulometry and voltametry.

Beginning about 1964, atomic absorption instrumentation was introduced initially for gold and magnesium determinations. From that date forward, many other applications were added. The development of the nitrous oxide burner (around 1968), and modifications permitting conversion of the instrumentation for flame emission spectrometry, hastened the process by expanding the capabilities of the method and, by the early seventies, elements as diverse as aluminum, arsenic and silicon were being determined routinely with this instrumentation. The cold vapour absorption method for mercury was another application, and copper, nickel, lead and zinc were still others.

X-ray emission spectrography was used beginning early in the sixties, but was not applied routinely because of its low sensitivity at the time, as well as a lack of suitable techniques for overcoming inter-element and matrix effects. By 1972, suitable correction procedures had been worked out so that, by using a procedure such as dissolution or fusion to homogenize samples, analyses could be performed that provided good precision combined with speed.

Comments on the relative merits of analytical methods for heavy metals, and potential sources of error, are included in Section 3.3 below.

Purpose of Analytical Work of the Radioactivity Division

From its beginning around 1946, the objective of the Radioactivity Division and its successor, the Extraction Metallurgy Division, was to develop metallurgical treatment processes for the recovery of first, uranium, and then other constituents from ores. Environmental studies were not included in the objective. Thus, the purpose of the analyses provided was to provide the information to guide process development, to establish the extent of recovery obtained, to provide analyses for control of the conditions being investigated, to provide data on the behaviour of undesirable impurities in the product, and determine whether it would meet commercial specifications.

In this connection, a distinction must be made between "tailings" and "tails". The former term is used by CANMET to indicate the total flow sent to the tailings pond, while the term "tails" is used to refer to the actual solid leach residue (or barren waste rock in the case of physical separations).

The "tailings" from a mine includes as well the soluble loss and the solids precipitated from the barren solution which forms the liquid portion of the tailings slurry. It was never analyzed at this laboratory as such, although the constituents of interest, from a process point of view, were. The same situation would apply to the mines up until the time they would have been required to do so by the regulatory authorities.

Comments Regarding Estimates of Precision

Although it is possible to provide an indication of the precision an analytical method is capable of, it does not necessarily follow that that precision was achieved (or in some

cases was not exceeded). A painstaking and skilful analyst can achieve remarkable precision, given time. On the other hand, both in process development and plant operation, a quick approximate value may be more useful than a more accurate one received a day later. At the mines, of course, monthly composites were given special attention, and the precisions indicated are probably realistic.

The term "% relative standard deviation" used here means the standard deviation as a percentage of the constituent concentration (also in percent) in the sample, i.e.:

where x = % concentration and $\bar{x}$ = mean of n samples

$$\frac{\left[\Sigma (x-\bar{x})^2/(n-1)\right]^{1/2}}{\bar{x}} \times 100 = \% \text{ relative standard deviation}$$

Chronology of Process Development Work at the Mines Branch

Uranium and Thorium

1946:	Establishment of the "Eldorado Project".
1947-1949:	Development of the Port Radium acid leach process.
1949-1950:	Development of the Beaverlodge carbonate leach process.
1951-1956:	Pilot plant investigations on ores from the Beaverlodge area, the Bancroft area and the Elliot Lake area; and development of ion exchange processes.
1956-1958:	Development of solvent extraction processes.
1958-1962:	Studies on thorium recovery from Elliot Lake solutions. Bacterial leaching studies. Studies on pre-concentration of uranium in ores.
1966-1972:	Optimization studies on existing processes, Elliot Lake ores. Use of pressure leaching, Elliot Lake ores. Assistance to Agnew Lakes with respect to in-situ bacterial leaching.
1972-	New processes to reduce environmental impact.

Methods Used to Evaluate Precision and Accuracy

Uranium and Thorium "Standard" Samples

Initially, the primary standard obtained around 1947 was the Madison Square standard - pure U_3O_8, 99.5%. A few samples of Port Radium pitchblende (approximately 50% U_3O_8) that had been repeatedly analyzed were also used for estimation of method precision. Standards of low grade materials were obtained from the National Bureau of Standards samples (later distributed by New Brunswick Labs, U.S. AEC). These included phosphate rock - 0.029%; low-grade pitchblende - 4.29%; carnotite no. 4 - 0.18%; carnotite no. 5 - 0.11%; and monazite sand - 0.38%. A large sample of monazite prepared by Eldorado labs was also used after careful internal analyses.

Beginning about 1949, extensive suites of low-grade samples, for use by prospectors and mines as radioactive standards, were prepared by diluting pitchblende with representative rock types. The extensive replication involved in verifying their uranium content served also as a method of internal quality control. U_3O_8 content ranged from 0.026% to 19% and higher.

In 1960, a program to prepare standard ore and tailings samples from all the Canadian mining areas was initiated under the auspices of the Canadian Uranium Producers Analytical Subcommittee comprised of about 16 samples of ores and tails. The Radioactivity Division participated in the certification analyses program. This activity lasted until 1962. The supply of these standards became depleted around 1970 and a second series of standards was produced. This program was handled by the Extraction Metallurgy Analytical Lab itself and, in addition to about five Canadian laboratories, five foreign laboratories also participated. These standards ranged in concentration from 0.004% to 1.0% U_3O_8, and from 0.001% to 0.11% ThO_2 (Ingles et al., 1977). An additional standard, 7.1% U_3O_8, was certified in 1979 (Faye et al., 1979). The laboratory also participated in other exchanges, e.g., within the Eldorado group, with the Commission on Radioanalytical Chemistry and Nuclear Materials of the International Union of Pure and Applied Chemistry (IUPAC, 1971) and with the Australian Atomic Energy Commission, also in 1971 (Florence et al., 1972).

Other checks on accuracy and precision consisted of periodic resubmission of previously analyzed samples, and replications of analyses by several different analysts.

Data Handling

Calculations were performed manually, either using logarithmic transformation or a large cylindrical slide rule with spiral ruling. About 1952, mechanical calculators replaced these techniques and, by 1956, electronic calculators were being used. Results were recorded in a large log book and reported immediately to the originator of the sample.

Beginning about 1970, x-ray emission data were processed by computer because of the complex correction equations employed, although some of the correction procedures could still be handled on a desk calculator.

3.2 Sample Collection and Handling

3.2.1 Goals

Sampling is a critical step in the process of outlining the characteristics of a system of which little is known. Collection of environmental samples poses unique problems in that no true and reliable standard techniques are applicable to all sampling situations and types of parameters. In addition, environments such as uranium tailings are heterogeneous and dynamic (water and air) adding to the potential for lack of representation of the system by the collected samples. Because of the problems that sampling poses, and because this procedure is unglamourous and frequently inconvenient, it has often proven to be the weak link in the chain of data acquisition. It is now recognized that a number of questions must be addressed prior to conducting a sampling operation.

The first aspect of any sampling program is to define the nature of the sample. This may seem self-evident, but is often overlooked in sample collection programs. As an example, one can consider the sampling of stream water. What type of sample is desired? If the sample is collected as a grab sample, does it represent a specific time of day, or can it reliably be accepted as representative of the day, week or month? If the

water contains suspended particulate matter, which phase is more important, if any? Does the sample represent the whole length of the stream of interest and, if not, what distribution of samples along the stream is needed to describe the parameters of interest? Answers to these questions pertaining to heterogeneity and dynamics are necessary to determine specifically what the sample represents.

After deciding on the appropriate sample, it is then necessary to maintain the integrity of the parameters of interest within the sample. In some surface environments, this does not necessarily impose problems. In many other environments, however, the sampling procedure, including exposure to the atmosphere, leads to rapid deterioration of certain properties. This problem may be overcome by either conducting the desired measurement or analysis in the field, or by preserving the sample in such a way as to minimize deterioration. Therefore, it is necessary to specify the desired parameters prior to sampling, and then to develop a sampling strategy that would be used in the field. In addition to the potential for degradation due to changes in environmental conditions, care should also be taken to ensure that sample containers and sampling equipment are compatible with the parameters chosen for analysis. This is especially important for trace chemical constituents that may be subject to adsorption to or release from the material that the sample container is composed of. A few manuals are now available that stipulate preservation techniques and preferred materials for a large variety of chemical species, both in water and gas phases (EPA, 1977; Environment Canada, 1983; Gillham et al., 1983).

3.2.2 Sampling Concerns for Uranium Tailings

Sampling of uranium mill tailings can be categorized into three broad areas. These consist of solids, water and air. Each of these categories can be subdivided into more specific areas of interest. For solids, these areas include mineralogical and chemical compositions, physical properties and, on a larger scale, the hydrogeologic characteristics that control the movement of pore water through the tailings. Water includes subsurface pore water, as well as that on the surface of the tailings and localized seepage found at the base of retaining structures. Other measurements include the pressure and piezometric heads that determine the flow, water levels in streams and stream flow values. Air samples would include those for radon gas, as well as for particulates above the tailings. Pore gases are also important - for example, the partial

pressure of oxygen is a significant control upon the rate of pyrite oxidation in the tailings. Because of the diverse nature of the sample types, and because various sensitive parameters exist for each of these types, any description of sampling procedures would require a lengthy discussion. Notes on such procedures can be found in the manuals cited above. The following discussion will focus only on general precautions in the areas described above.

3.2.2.1 Solids

In general, standard methods can be used to measure the physical characteristics of tailings. Qualities such as dry bulk density, particle density and moisture content can be measured following set techniques. Chemical and mineralogical characterization would also be fairly standard, except that special attention would be given to radiological species.

The quality of such samples would appear to depend on the extent of descriptive field notes associated with these samples. Because the tailings are generally heterogeneous, both physically (layered, coarse and fine) and mineralogically (bands of concentrated pyrite grains), it is important to know what exactly is represented by a sample result. For instance, the grain-size distribution representing a large depth-scale sample would not likely indicate the presence of a relatively thin slime layer. That layer, however, would probably be the controlling factor in the movement of pore water, as well as the movement of important gases such as oxygen (for pyrite oxidation) and radon (exhalation at the surface).

3.2.2.2 Water

The complex chemical composition of water, as well as the diversity of sampling environments, in and around the tailings impoundments suggests that standard sampling techniques may not be applicable. Various methods and sampling devices have been described. Each method has both positive and negative aspects, and the ones used should be judged on the basis of applicability to the appropriate problem.

A specific concern of sampling the chemical composition of water is knowing whether the results represent the dissolved load only or the total load, including suspended

particles. In stream sampling, both the suspended and dissolved components are important, with respect to transport processes. However, these components behave differently and should be clearly distinguished. In subsurface pore water, only the dissolved component is generally considered and, therefore, all such samples should be filtered before analysis. When analyzing for metals and radionuclides, the samples should be acidified, following filtration, to minimize precipitation and adsorption. Sample processing normally occurs in the field immediately upon collection. This is particularly important when sampling pore water, or dissolved species in anoxic or slightly acidic surface water, where some species would be expected to become unstable after collection. Ascertaining the quality of results based on sample techniques requires that the methods, equipment and sampling protocol be stated for each data set. Data that has no indication of methodology should be regarded with caution.

The collection of water level data from piezometers that are used to determine the groundwater flow characteristics is rather standard. The quality and representativeness of the data are more dependent on the devices used and the method of installation than on the measurements of water depths. Again, descriptive field notes are an important criteria for determining the quality of data generated.

3.2.2.3 Air

The sampling of airborne particulates to assess air quality involves standard techniques to measure suspended matter and dustfall. Radon sampling usually includes analysis directly in the field. Therefore, instrument calibration and descriptive field notes on weather conditions increase the confidence level attributed to the quality of the results.

Radon exhalation to the atmosphere is expected to occur from tailings derived from all types of uranium ores. The flux of radon at the surface will be a function of the activities of radium (parent) present in the tailings, as well as the movement of radon gas toward the surface of the tailings. In general, radium has a tendency to be concentrated in the fine or slime fraction of tailings and, hence, one would expect there to be higher levels of radon gas associated with areas containing a large fraction of fines. As a gas, radon will be transported through the porous tailings in a number of ways.

One mechanism responsible for radon movement would be diffusion. Because diffusion usually results in low fluxes, and because the half-life of radon is on the order of four days, only the radium that is decaying close to the surface is likely to contribute to radon exhalation through this process. In coarse-grained tailings, significant drainage of water is likely and diffusion of radon would occur mostly through the gas in the pore spaces. This would likely represent a relative maximum for the rates of radon movement by diffusion. Even then, however, fluxes would remain low, and only shallow surface zones in the tailings would affect radon exhalation. In finer-grained tailings, pore spaces would retain greater percentages of water and, with diffusion of gas being about four orders of magnitude less in water than in air, transport of radon would be further retarded. In fine tailings and/or wet zones, the effective depth from which radon is generated and exits the surface by diffusion is likely to be quite small.

A second mode of radon transport in the porous tailings involves changes in barometric pressure. The gas in the pore spaces above the water table expands and contracts in response to atmospheric fluctuations. Upon increasing barometric pressure, atmospheric gas is compressed into the top zone of the tailings. During that time, radon would be continuously generated and released to the gas in the pores. When the pressure decreases, the gas expands and the excess near the surface would exit to the atmosphere. This "barometric pumping" is a cyclic process that would likely be more effective in transporting radon to the surface than diffusion. The depth within the tailings affected by this pumping depends on the depth to the water table. Because this process obeys Boyle law, and because atmospheric fluctuations are rarely greater than 5%, the affected zone would be limited to about 5 cm for every metre that the water table extends below ground surface.

A third mechanism of radon transport in the tailings involves the infiltration of moisture. When rainfall or snowmelt occurs, the water moves downward into the pore spaces that are partially filled with gas. The gas existing in a particular zone will be displaced by the water as it moves through that zone. This will cause the gas, that occurs near the surface, to exit to the atmosphere or dissolve. More significant displacements of gas will occur with greater quantities of infiltration, so that it is expected that this process is most effective during spring melt and during the rainy autumn season.

From the above points, it is apparent that radon concentrations at the tailings surface will fluctuate spatially due to source and moisture condition, as well as temporally due to seasonal and diurnal changes. These factors should be considered in the design of the sampling program and in interpretation of the results. Field notes should include grain size, barometric pressure and substrate moisture profiles.

3.2.2.4 Field Measurements

Important surface water parameters that should be measured in the field include pH, specific conductance, dissolved oxygen, temperature and transparency. The following outlines some important considerations in measuring each of these parameters.

Measurement of pH in the field requires considerable care. Electrodes and buffers must be equilibrated to the same temperature as the water to be measured. The electrode must be calibrated with buffers that bracket the pH of the sample, and must be rinsed with distilled water after immersion in each buffer or sample to prevent cross-contamination. After each pH reading, the pH of the buffers should be checked and only if they have remained stable within 0.02 units should the pH of the sample be accepted. Perhaps the most important consideration in measuring pH is to carefully review the instruction manual of the meter and electrode if the scientist/technician is not completely familiar with their use. Stabilization of electrode temperatures prior to reading, insulation of the instrument from the ground and protection from direct sunlight are usually recommended.

The specific conductance is readily determined by inserting a conductivity probe into a water sample and reading the conductance on an appropriate meter with an alternating current applied between two electrodes in the probe. The probe and meter must be calibrated in a sample of known conductance at 25°C (generally 0.01 M KCl) before they are used in the field. Because conductance changes markedly with temperature, the temperature compensator on the meter must be adjusted to the temperature of the sample before the reading is taken.

Dissolved oxygen is measured in the field, either using a dissolved oxygen meter and electrode, or the Winkler titration method. The electrode procedure is more quickly carried out than the Winkler method, but is probably less accurate (± 1 ppm vs. ± 1 ppb).

Dissolved oxygen meters and probes must be carefully calibrated, generally immediately before use. In addition, the integrity of the membrane on the electrode should be checked before use and replaced if an air bubble is present in the probe, or if the membrane itself appears damaged or contaminated. During the course of a survey, the meter and electrode should be re-calibrated periodically. If maximum precision is not of major concern, the meter may be calibrated with air-saturated distilled water of known temperature and a table of dissolved oxygen concentrations at saturation. Other standards may be prepared to improve the calibration, such as the $FeCl_2$ standard described in the University of Waterloo short course on "Field Methods in Contaminant Hydrogeology" manual (Cherry et al., 1984). Occasional samples for Winkler titration may also be taken to calibrate the meter. If not completely familiar with its use, the technician/scientist should review the instruction manual for the meter.

The Winkler procedure for dissolved oxygen determination, unlike the electrode method, requires that the sample be brought to the surface and transferred to a glass-stoppered bottle. Care must be taken that the sample is not allowed to bubble in the air. Several (3-4) volumes of sample water should be allowed to flush through the bottle, and the bottle is then stoppered carefully so that air bubbles are excluded. The next step involves the addition of reagents (manganous sulphate and alkali-iodine-azide) followed by acidifcation and titration with sodium thiosulphate (see the American Public Health Association's "Standard Methods for the Analysis of Water and Wastewater", 15th edition (APHA, 1980)). While the Winkler procedure can provide a relatively precise dissolved oxygen measurement, it is subject to interference from nitrite, ferrous and ferric iron, sulphite, sulphide and polythionates. "Standard Methods" should be consulted for modifications to the Winkler technique to adjust for interfering substances. Probably the most common source of error in applying the Winkler technique is improper preparation of the sodium thiosulphate used for titration. Its concentration must be precisely known to provide a precise oxygen measurement.

Temperature is measured in the field, either by hand-held thermometer or, more commonly, with a dissolved oxygen-temperature meter or a conductivity-temperature meter. If accurate temperature readings are required, the readings given by the meter intended for use should be first checked against an accurate thermometer.

Water transparency is typically measured with a black and white metal disc, known as a Secchi disc. The disc is lowered into the water column until it just disappears. It is then raised slowly until it just reappears. The half-way point between disappearance and re-appearence is recorded as the water transparency, and is usually expressed in metres. Although widely used to measure transparency, the Secchi disc is often used incorrectly. It should be lowered from the shaded side of the survey boat and the observer should view the disc with his face as close to the water surface as possible. In addition, measurements should generally be taken within two hours of noon. Transparency measurements are subject to considerable variability due to the roughness of the water surface, cloud cover and the eyesight of the observer. In spite of their variability, transparency measurements show meaningful correlations with other water quality parameters, such as chlorophyll a content. Field notes on cloud cover and water roughness help the user to judge the significance of individual outlier values.

3.2.3 Sampling Documentation and Continuity

3.2.3.1 Documentation of Sampling and Handling

The choice of sample collection and treatment methods will depend on the sample type (i.e., surface water, seepage, pore water) and the purpose for which the sample is collected (i.e., to ascertain dissolved or total radionuclide load). Consequently, there is no single ideal protocol. For modelling purposes, the main concern is that protocol should be appropriate to the intended use and interpretation of the data. Information concerning sample type, location, collection and treatment methods, and field conditions should, therefore, be available to potential users of the data.

While some of this sampling information is included in the CANUT database, it would not be convenient to incorporate all relevant details of methodology and field conditions. However, identification of the organizations responsible for sampling and sample handling, and a sample reference number, would enable the user to request additional information, if available. The importance of sampling documentation, including the chain of sample custody, is emphasized by Keith et al. (1983).

Documentation of such information in the field log could be used as a convenient criterion of data quality. Sampling and handling would then be evaluated with reference to a checklist such as follows:

Field Log Entry			Numerical Value
Sample Type			0/1
Location		-position, depth	0/1
Collection Methods	-	equipment, flushing, etc.	0/1
Treatment Methods	-	preservation	0/1
	-	filtering	0/1
	-	storage	0/1
Field Analysis	-	pH, Eh	0/1
	-	specific conductivity	0/1
	-	temperature	0/1
	-	dissolved oxygen	0/1
	-	flow	0/1
Chain of Sample Custody			0/1
Qualifications of Field Staff (none/technical or professional)			0/1

Certain items on the checklist may or may not be applicable, depending on the sample type. For example, the treatments and some of the field analyses listed would not be appropriate to air samples. Failure to document an applicable item on the check list would result in a score of 0 for that item. A score of 1 would be assigned for each adequately documented or inapplicable item.

A composite sampling and handling score between 0 and 1 could be computed from such a checklist, as the sum of scores, normalized to a convenient maximum value. Any sample with a score less than the maximum should be considered suspect on the basis of inadequate sampling documentation. The database user may still find it necessary to enquire about aspects of sampling protocol relevant to his particular needs, but could at least confine his enquiries to samples for which adequate documentation is known to be available.

Few, if any, of the historical samples represented in the CANUT database could be given a perfect quality rating on the basis of currently available sampling and handling information. However, sampling programs underway at present, or planned for the future, could easily be designed or modified to ensure documentation of all required sampling information.

3.2.3.2 Continuity of Sampling and Field Measurements

For long-term predictive modelling purposes, an understanding of both spatial and temporal variation in measured parameters is essential. This understanding is incorporated into the predictive process either in the form of probability density functions associated with each parameter in a stochastic model, or in defining boundaries for systematic variation of parameters during sensitivity analysis of deterministic models. An understanding of temporal variability can only be achieved by a continuous sampling program with repeated measurements at the location and over the time period of interest.

The continuity of the sampling effort, as represented in any database, can be assessed from the frequency of repeated measurements for a particular parameter at a particular location. Similar assessment techniques could be applied to chemical parameters or associated field measurements. For chemical parameters, concentrations measured in differently treated samples must be considered different parameters. Likewise, field measurements by different methods, such as automatic versus manual stream flow recordings, should be considered different measurements.

Consideration of sampling continuity as an aspect of data quality stretches the definition of "quality" to include the concept of "quantity". However, both concepts are relevant to the usefulness of the data for statistical modelling purposes. The logical distinction between these concepts should probably be retained by development of a separate evaluation criterion to represent the continuity of the sampling program. This criterion will be of particular use to the stochastic modeller in retrieving sets of repeated measurements, and should be defined in relation to the data requirements of particular modelling applications.

A sampling continuity factor could be calculated by normalizing the frequency of repeated measurements against some maximum value considered adequate for characterization of the probability density function within a particular region or time period. For example, if 50 measurements are considered adequate, 20 measurements of dissolved As concentration at the same location would each receive a continuity score of 0.4. Fifty or more measurements would all be assigned a perfect score of 1. Scores could

change with addition of new data to the database or with the modelling requirements of the user, and would have to be recalculated periodically.

3.2.4 Streamflow Records

Any long-term modelling of the geochemical behaviour of radionuclides and trace elements from uranium mine tailings requires an understanding of the mass balance of the particular element under consideration. In order to obtain mass balance data, it is necessary to know both concentration and flow information. The following section presents a discussion of flow data as measured for environmental samples in Canada.

Description of Methods

Streamflow data are available from a variety of sources including Federal and Provincial government agencies as well as various private organizations. In spite of the diversity of sources, manual hydrometric methods have not changed appreciably in historical time (Environment Canada, 1982). Automatic continuous recording gauges of the float and drum type have been widely used since the mid-1900's. More recently, pressure transducer gauges have become available, but these are not yet widely used.

Manual and automatic methods are used for recording flow information, either singularly or as a combination. The manual method relies on a vertical gauge staff calibrated in centimetres which is located at the station on the stream bank. The total length of the staff must exceed the maximum expected flood level. An individual operator normally makes one or more observations of the flow stage (stage being the water surface elevation) per day to obtain a daily mean value (Bruce and Clark, 1966; Environment Canada, 1982).

The automatic method relies on a continuous water elevation or stage recorder. The stage is recorded on a roll chart for periods of up to one year in duration. The recorder is usually situated on the river bank so that it is protected from flooding and/or ice damage. Manual gauges may also be located at a recorder site so that data accuracy and equipment operation can be periodically assessed (Bruce and Clark, 1966).

At each gauge site, it is necessary to measure water depth for at least 20 points across the river section; flow velocity at each depth profile; air and water temperature; and/or ice thickness when appropriate (Ozga, 1979). For larger rivers, more than 20 depth measurement points are advisable.

The repeated measurement of the noted variables yield information on the stage and discharge for the construction of a stage-discharge rating curve. Thus, for each stage observation, one can interpolate a corresponding discharge from the rating graph. Periodic checking of discharge is necessary to confirm the validity of the observations and the record.

If changes in flow conditions are obvious, or if the measurements versus the rating curve deviate significantly, then the stage-discharge relationship has to be redefined (Bruce and Clark, 1966; Environment Canada, 1982).

Sources of Error

Error can be associated with the hydrometric method that is used or with general and specific field conditions near the gauge site.

There are two major disadvantages associated with any form of manual gauging. Firstly, the reliability of the record is entirely dependent on the accuracy of the operators' measurements. In some cases, erroneous observations can escape detection from the record. Secondly, measurements are normally taken one or more times per day. Periodic measurement poses a serious problem since discharge in a stream can change dramatically over a short space of time. It is possible, therefore, that a major flow event or other variations in discharge will not be recorded. The result will be a distorted record of daily and perhaps monthly average discharges (Bruce and Clark, 1966). The aforementioned problems are eliminated with the use of a continuous recording device, since all flow levels are recorded.

Regardless of the method employed, one of the most critical factors affecting the validity of a flow record is control. Control refers to the downstream conditions that will influence the stage-discharge relationship at a gauge station. Rapids, lakes, weirs and dams, in addition to channel morphology changes, are factors that affect control. Where control is deemed to be stable, then the stage-discharge relationship will be

stable. However, changes due to erosion or deposition, or changes in base level and so on, necessarily result in control changes. Where the control is unstable and subject to change, frequent discharge measurements become necessary to allow for modification of the rating curve for a station. Accuracy in this case becomes a function of the frequency of repeated measurements (Bruce and Clark, 1966; Environment Canada, 1982).

At a station, ice conditions influence the accuracy of flow data since the flow regime is altered when compared to an open water state. Ice cover, stream intersections, dams and lakes cause a backwater effect that must be compensated for, by assessing water slope as a third variable, to obtain the appropriate stage-discharge relationship (Bruce and Clark, 1966).

The ideal point for measurement is where a channel constriction forms a hydraulic control point (Chow, 1968) in which flow passes from subcontrol flow (upstream) to supercontrol flow (slightly below the measurement point). This point controls the water level directly above it and is not influenced by flow immediately downstream. V-notch weirs and similar devices are inserted in small streams to create these conditions (Scheider et al., 1983). In large streams, such weirs are impractical, but judicious selection of a natural constriction gives some of the same flow characteristics.

Accuracy of Streamflow Records

The validity of streamflow data is difficult to assess since site-specific conditions, control, method of observation and frequency of measurement can and do vary between gauge sites (including multiple sites on the same stream system). As noted above, where control is good, a continuous recorder should yield data that are accurate to within 5% of the true value (P.I. Campbell, verbal communication, 1984). In fact, 5% error is probably an overly optimistic estimate. Personnel with the Saskatchewan and Ontario Environment ministries have suggested that an accuracy level of 10% to 15% would be more appropriate. Where control is poor, observations are manual and measurement infrequent the error could reach 50% (P.I. Campbell, verbal communication, 1984). More reliable, site-specific estimates can be obtained from Environment Canada and the relevant Provincial agencies.

Utilization and Evaluation of Flow Data

Existing published records yield daily, monthly and annual mean discharges. For appraising long-term trends or for modelling discharge patterns as a predictive tool, the monthly mean discharges are the most appropriate measures of flow. Monthly averages reflect seasonal trends whereas sporadic daily measurements may not.

The major problem in using hydrometric data is the length of the record. In many cases, continuous recording at a station has been restricted to the last 25 years. A long record is preferred since trends in flow characteristics or environmental controls may be evident from the flow data. For records of ten years or less, there may not be any indication of long-term flow trends and estimates of annual and seasonal variability may be unreliable.

Aquatic dispersion modellers should be aware that flow records may be 5% to 50% in error, depending on flow conditions and control. The Ontario Ministry of the Environment and the Saskatchewan Ministry of the Environment have assessed the methods and records associated with various sites. Personnel in both agencies have suggested that true discharges should usually be within 10% to 15% of the recorded data. Unfortunately, these estimates cannot be generally applied to all stations.

Finally, the general concensus is that manual gauging has a potential for low or uncertain accuracy when compared to the more reliable continuous recorder gauge. This factor can be considered as part of the field analysis program in evaluation of sampling and handling. For specific stations, it is possible to obtain accuracy estimates from the Water Survey of Canada (Environment Canada) or other monitoring organizations.

3.3 Laboratory Analytical Methods

Methods of Analysis for Radionuclides

Methods of analysis for radionuclides arising from the uranium and thorium series are described below, with brief comments on their relative merits and potential sources of error.

Ra-226

The two main methods for determining Ra-226 are the barium sulphate coprecipitation method, and the Rn-222 emanation method. Both rely on gross alpha counting. As noted later, improvements are possible by use of alpha spectroscopy. The first of these two methods is subject to a positive interference from Ra-223 arising from the U-235 series. Given that the ratio of U-238:U-235 is normally 140:1, this positive error is small, equal to 4.4% for an ingrowth period of six days. The error varies with ingrowth period as follows: 17.4% at 1 to 5 hours, 11.8% at 1 day, 8.7% at 2 days, 6.9% at 3 days, 5.7% at 4 days, and 5% at 5 days. It should be noted that waste streams which have been treated to coprecipitate radium in a barium radium sulphate may have levels of Ra-223 many times higher than those of Ra-226. In such cases, the emanation method is preferable. Additional positive error arises from the presence of Ra-224 from the natural thorium series (Th-232). If natural thorium is involved, differential decay corrections for the presence of Ra-224 are required. Such corrections would need to be considered for Ontario samples originating from the Elliot Lake region. In the absence of a statement of correction in published data or reports, it should probably be assumed that such correction was not made. The precipitation method allows a greater rate of throughput of samples than the emanation method.

The emanation method for Ra-226 is based upon a count of the Rn-222 allowed to grow for a specified time (normally 5 to 7 days) in a solution stripped of dissolved radon prior to the growth period. The Rn-222 is subsequently counted using a ZnS scintillation detector. This method is much less sensitive to the presence of Ra-223 than the method using coprecipitation and gross alpha counting. For example, in the latter method, a 100:1 ratio of Ra-223:Ra-226 would result in an error of 2300% if the sample were counted after a six-day ingrowth period, and all activity assumed to be from Ra-226. After a six-day ingrowth period in the emanation method, on the other hand, the error would be less than 8%. The presence of high levels of Ra-224 would result in similar errors for the two methods. Thus, for samples such as mill discharges having an abnormally high ratio of Ra-223 to Ra-226, or for samples containing high levels of Th-232, the emanation method is preferred over the coprecipitation method.

Alpha spectroscopy may be used with the coprecipitation method to reduce interference from other Ra isotopes. The 4.8 MeV peak of Ra-226 is counted. It is important that a

thin precipitate source on the filter be used so that self-absorption is small. Self-absorption can be corrected to some extent. This method is the most selective of the Ra-226 methods.

Ra-228

Determination of Ra-228 (arising from the Th-232 series) is more difficult because it emits only weak beta particles. The preferred procedure is to separate all the radium isotopes by coprecipitation with lead sulphate followed by coprecipitation with barium. A period of 24-36 hours is then allowed for Ac-228 to ingrow from Ra-228. The beta energy from Ac-228 has a maximum of 2.1-2.2 MeV, compared to ≃ 0.05 MeV from the parent Ra-228. Ac-228 is more readily measurable by beta counting with either a proportional counter or a beta phosphor-photomultiplier detector.

Pb-210

Likewise, Pb-210 (arising from the U-238 series) is a weak beta emitter (about 0.06 MeV maximum). It is determined from its daughter Bi-210 (beta 1.2 MeV maximum). Lead is solvent extracted from solution with diethylammonium diethyldithiocarbamate (DDTC) in chloroform from a 2 M HCl solution. Interfering elements (ferric iron, copper) are removed prior to extraction by reduction with ascorbic acid (ferric to ferrous) or pre-extraction with DDTC at higher acidity (8 M HCl). Bismuth is finally precipitated as BiOCl by addition of NH_4OH to pH 8. The precipitated filtrate is then counted. At least 30 days ingrowth is required for ≃ 98.5% equilibrium between Pb-210 and Bi-210. If a shorter ingrowth time is to be used, existing Bi-210 must be extracted and discarded in order to allow a definite ingrowth period for the Bi-210 from the Pb-210. About 18 hours are allowed to elapse before counting in order to allow the short-lived isotopes of bismuth (Bi-211, Bi-212, Bi-214) to decay. Because of the ease with which Bi is precipitated in natural waters, it is unlikely that Pb-210 and Bi-210 are in secular equilibrium in such environments.

Po-210

Po-210 is determined by alpha counting after spontaneous deposition onto silver metal from HCl solutions. Either gross alpha counting or spectroscopic alpha counting may be

used. Although traces of isotopes of bismuth and lead may codeposit onto the silver with polonium, only bismuth has an alpha emitting isotope of long enough half-life to be a potential interference. Because Bi-212 has a half-life of 60.5 min compared to 138.4 days for Po-210, a delay of 24 hours before alpha counting is sufficient to remove interference from the Bi-212. The method is, therefore, extremely specific for Po-210. Detection limits for alpha spectroscopy are lower than for gross alpha counting owing to a lower background.

Total Thorium

Total thorium may be determined fluorometrically by complexation with morin or, preferably, spectrophotometrically by complexation with arsenazo III (1,8-dihydroxy-naphthalene-3,6-disulphonic acid-2,7-bis(azo-2-phenylarsonic acid)). In preparation for analysis, thorium, along with other large ions, is separated from other cations by coprecipitation with lead sulphate, and then separated from a diethylenetriamine-pentaacetate solution of lead sulphate by extraction into bis(2-ethylhexyl) phosphoric acid, and finally back extracted into an aqueous solution of oxalic acid for spectrophotometric determination with arsenazo III. Analysis of the thorium-arsenazo III complex is conducted in a 3 N HCl solution at 665 nm in the visible band. There are no known interferences.

Thorium Isotopes

Th-232 and Th-228 from the thorium series and Th-230 from the U-238 series can be determined separately by high resolution alpha spectroscopy. Thorium is pre-separated from other elements as before, and precipitated onto a membrane filter as the hydroxide with a cerium hydroxide carrier. Self-absorption correction may be required if the precipitated deposit is thick.

Uranium

Several methods are available for the determination of uranium. Two important methods are based on fluorimetry and spectrophotometry. The fluorometric method is based upon the fluorescence (yellow-365 nm) of uranium fused with sodium fluoride. The many interfering elements are handled by removal of uranium as uranyl nitrate into ethyl

acetate or methyl isobutyl ketone. In the spectrophotometric method, a complex is formed between uranium and bromo-PADAP(2-(5-bromo-2-pyridylazo)-5-diethylamino phenol) in an ethanol-water mixture at pH 7.6 and in the presence of a mixed complexing solution containing 1,2-cyclohexylene-dinitrilotetraacetic acid (CyDTA), sulphosalicylate and fluoride. Measurement is normally at 578 nm. Interfering species are eliminated by the special complexing conditions or by extraction.

Methods of Analysis for Heavy Metals (Non-radionuclides)

Of the enormous variety of methods of analysis, the methods most useful for heavy metal analysis are the atomic spectral methods (absorption - flame and electrothermal; emission - spark, arc, flame and inductively coupled plasma; and fluorescence - flame, electrothermal and x-ray), and neutron activation. Of the atomic spectral methods, flame absorption spectroscopy has until now been the most commonly used method for routine analysis, particularly of heavy metals. High specificity is possible, but most readily for one species at a time. Interferences are well known and can be handled by standard methods. Atomic emission spectroscopy is particularly well suited to analysis of low atomic number elements and can be used with computer-controlled monochromators and optical multi-channel analyzers which acquire data for several elements simultaneously by scanning the spectrum.

Inductively-coupled plasma (ICP) source emission spectroscopy is a relatively recent development. Typically, an inductively coupled radio frequency field ionizes a stream of argon gas; the sample is injected into the high temperature plasma produced by excitation by the externally applied field, and produces a characteristic emission spectrum superimposed on that of argon. Fewer interferences are present compared to flame emission systems, largely because of the high plasma temperature. Simultaneous multi-element analysis is possible, and detection limits are comparable to or better than other atomic spectral methods.

Long wavelength UV fluorescence may be used to analyze for uranium as noted in the discussion of methods of analysis for radionuclides. X-ray fluorescence is applicable to a wide range of elements, especially beyond atomic number 23 or so (below this atomic number detection limits progressively worsen). Matrix effects are of major concern, and require special attention, including such measures as use of a standard in the same (or

closely similar) matrix, use of internal standards, and dilution of sample and standard. Simultaneous multi-element analysis is possible.

Neutron activation followed by gamma spectral analysis is probably the most sensitive method of analysis for most elements in the Periodic Table (excluding light elements). A few elements are either not amenable to analysis (e.g., Pb) or not particularly suitable (e.g., S). A major advantage of neutron activation analysis is that simultaneous multi-element analysis is the normal mode of operation. Most interferences can be handled readily. Occasionally, a high level of one element may make determination of low levels of another difficult. Major disadvantages of neutron activation analysis are the large capital and operating costs associated with the reactor required for the work (in Canada, a SLOWPOKE reactor).

Documentation of Methodology, Staff Qualifications and Performance

The choice of analytical methodology usually depends upon the purpose of the analysis (sample type, level of activity and degree of accuracy or precision required). Analyses for the purpose of process control, for example, must be performed rapidly and cost-effectively, but need not be highly accurate or precise. On the other hand, environmental analyses for the purpose of human health protection must be extremely accurate and precise at low activity levels. Both analytical approaches can provide useful information for environmental modelling purposes. However, the modeller must be able to distinguish between them in order to make reasonable assumptions regarding accuracy and precision.

Since it is not practical to incorporate detailed descriptions of analytical methodology into a database, the laboratory responsible for analysis of each sample should be identified in the database, and should be able to document its methodology on request. The importance of analytical documentation is emphasized by Keith et al. (1983).

Laboratories for radionuclide analyses were evaluated in terms of methodological documentation, staff qualifications and performance in interlaboratory studies. The criteria chosen for evaluation were quantified from the responses to the questionnaires (Appendix 2), taking the information given at face value. All evaluations are based on current laboratory practice due to a general lack of historical information in laboratory

responses. Josephson (1984) gives a good example of this type of general laboratory evaluation based on similar criteria.

The criteria selected (see Table 3.5) were in general assigned a maximum point score, and the laboratory in question awarded or not awarded points based upon its response to the questionnaire. This procedure was followed for criteria A-C. In the case of criterion D, the results of the CANMET interlaboratory comparison (Radioisotope Activities in Uranium Tailings Reference Materials UTS-1 to UTS-4: Results of an Interlaboratory Comparison", C.W. Smith, Chemical Laboratory, CANMET, August 1983, MRP/MSL 83-112 (TR)) were examined. Since the true value of an analytical standard is rarely known and since a simple interlaboratory average would not allow for possible systematic laboratory biases - only the intra-laboratory analytical variation was analyzed. For each of the radionuclides analyzed, each laboratory was ranked in order 1 to 8 (for the eight participating laboratories) in order of increasing standard deviation of their replicate analyses. Analyses showing only two measurements were excluded. The average laboratory rank for all methods was then determined, and this converted into a point score normalized in the range 0-4, and rounded, with 4 being the "best" score. These normalized points are those recorded in Table 3.5. Criterion E provides an alternative score for laboratories, which participate in other interlaboratory comparisons. Laboratories would be assigned a score for criterion D or E, but not both. Thus, a laboratory which performed poorly in the CANMET study could improve its score by participating in other studies.

It should be observed that the relative weights chosen for the criteria A-E are subjective and, clearly, a different final result would occur for different weights. The weights chosen are not, therefore, defended in an absolute sense; rather, they are chosen as a best judgement. Further, the choice of the criteria themselves is also a best judgement. Beyond these judgements, however, the evaluation is objective.

A valid criticism which may be voiced is that from knowledge of a given laboratory and its personnel, one "knows" whether the results of that laboratory can be "trusted". To a considerable degree, this intuitive evaluation is likely to be correct. It cannot, however, be easily quantified, and is best left as an overlay for the individual reader to apply to the evaluations presented here.

TABLE 3.5: LABORATORIES FOR RADIONUCLIDE ANALYSIS - DOCUMENTATION OF METHODOLOGIES, STAFF QUALIFICATIONS AND PERFORMANCE

The laboratory rating scheme is based on the responses provided by the laboratory in the questionnaire survey, in some cases, subject to additional clarification. Each attribute of the laboratory is awarded points or not according to whether the laboratory has or does not have the attribute, or how it performed in terms of internal consistency only (not accuracy) in the interlaboratory comparison.

	Commerical Service Laboratories					Government Laboratories							Mining Industry Laboratories			University Laboratories		
Critera (points)[1]	No. 6	No. 7	No. 2	No. 3	No. 8	No. 29	No. 13	No. 17	No. 18	No. 20	No. 27	No. 33	No. 22	No. 23	No. 34	No. 25	No. 26	No. 28
A Use Externally Documented Methods (15) OR Use Internally Documented Methods Open to Review (3)	15	15	15	-	15	15	15	15	15	-	15	-	15	3	15	15 (?)	15 (?)	15
B Involved in developing (publishing) new methods (3)	?	?	3	3	-	3	3	-	-	-	3	3	-	-	3	3	3	3
C Highest level of education (1-3)	3	3	3	3	1	3	3	3	1	1	1	-	?	1	1	3	3	3
D Interlaboratory comparison of internal consistency, CANMET 1983 (0-4)	-	-	4	-	-	-	-	-	-	-	-	-	-	-	-	3	-	-
OR																		
E Participation in other interlaboratory comparisons (2)	2	-	-	2	2	-	2	2	2	2	2	-	1	1	1	-	2	-
	20	18	25	8	18	21	23	20	18	3	21	3	16	5	20	24	23	21

[1] Relative weighting of criteria according to the maximum possible point score represents a subjective judgement of importance.

C: 1 = B.Sc. or Technical College, 2 = M.Sc., 3 = Ph.D.

D: 0 = worst precision, 4 = best precision; poor performance can be offset by participation in other studies (E).

E: 1 = "umpire" program, 2 = formal interlab study.

The overall scores for the various laboratories should, therefore, be interpreted as only a guide subject to the arbitrary best judgements inherent in the criteria selection and weighting procedure. Since they are based on current laboratory information only, their application to judgement of historical data quality is limited.

3.4 Data Handling and Reporting

Procedures for handling and reporting data can be formalized and standardized to a greater extent than analytical procedures. Data from diverse types of analysis can be handled according to a single standard protocol which minimizes opportunities for human error. Up to a point, such protocol can be evaluated independently of the type of analysis or laboratory generating the data. This section outlines possible criteria for evaluation of data handling and reporting protocol, based on questionnaire responses of various analytical laboratories. A similar, parameter-independent laboratory evaluation system is described by Josephson (1984).

Questionnaire responses were taken at face value. Clarification was sometimes requested, but no attempt was made to verify the accuracy of the information supplied. Neither was the actual effectiveness of professed data handling protocol investigated.

Laboratories were asked to describe procedures for proof-reading reports and checking calculations. These activities are performed on the assumption that occasional errors in computation or transcription will occur and require correction. They should be performed by at least one person other than the technician performing the original analysis or calculation.

Ideally, several people should proof-read every report, independently, looking for internal inconsistencies in the data, values outside the normal range for a particular sample, correct reporting of significant figures and correct reporting of methodology. All calculations should be reviewed at least once.

Laboratories were also asked to describe any computerization in the data reporting protocol. Computerized data storage may contribute to quality control by minimizing the amount of data transcription required in report preparation. However, this is not necessarily the case. The main value of computerization is that the computer can also

perform logical checks for inconsistent or outlier values. The need for computerization is dependent on the amount of data to be processed. Also, logical checks for mutually exclusive or inconsistent values are more appropriate to some types of analysis than others, and may therefore be more applicable to certain labs.

Table 3.6 summarizes laboratory protocol with regard to data handling and reporting, and provides a possible basis for comparing various labs. Each column represents one aspect of data handling and reporting protocol, coded on a numerical scale. The highest scores for report proofing, calculation checking and computerization represent ideal protocol.

The coding scheme was developed a posteriori, based on laboratory responses, and was not presented with the questionnaire. It is possible, therefore, that some respondants could improve their scores by describing protocol in greater detail. Opportunities for comment on the criteria should be provided before final implementation of such a scheme for evaluation of data handling and reporting protocol.

A possible evaluation criterion is suggested by the composite score in the last column of Table 3.6. This score is simply the number of positive scores in the other columns, and has a maximum value of 3. It should be emphasized that the weighting system inherent in this scheme is subjective and implies a judgement of approximately equal importance for proofing, re-calculation and computerization. In view of their subjective component, scores should be considered approximate at best. They are based on current laboratory practice and should not be applied out of that context.

Some laboratories failed to provide any description of data handling and reporting protocol. This may imply that protocol is not good at present, as indicated by the NHRI response. The conservative approach would be to make this assumption. However, disagreement with the premises implicit in the selection of criteria for inclusion in this section of the questionnaire may also be involved. For example, Don Wiles of Carleton University has pointed out that computerized systems are not necessarily more reliable, as reflected in the scoring system of Table 3.6.

TABLE 3.6: DATA REPORTING PROTOCOL

Based on responses provided in the laboratory survey, subject to additional clarification in some cases. Laboratories with and without radionuclide capabilities included.

Laboratory	Report Proofing 0 none 1 single 2 double	Calculation Checks* 0 none 0.5 spot 1 all	Computerized Records 0 no 0 yes 2 logical checks	Composite Score**
No. 1	1	1	2	4
No. 2	1	1	0	2
No. 3	2	1	0	3
No. 4	1	0.5	0	1.5
No. 5	2	1	0	3
No. 6	2	1	0	3
No. 7	1	0.5	0	1.5
No. 8	1	0.5	0	1.5
No. 9	1	-	-	1
No. 10	-	-	-	0
No. 11	-	-	-	0
No. 12	2	1	0	3
No. 13	1	1	0	2
No. 14	2	1	0	3
No. 15	2	1	0	3
No. 16	1	1	0	2
No. 17	1	1	0	2
No. 18	1.5	0.5	0	2
No. 19	1	0.5	-	1.5
No. 20	-	0.5	0	0.5
No. 21	-	-	-	0
No. 22	1	1	-	2
No. 23	1	-	-	1
No. 24	1	-	2	3
No. 25	-	-	0	1
No. 26	1	0	0	1
No. 28	1	0.5	0	1.5
No. 29	1	-	0	1
No. 30	1	-	2	3
No. 31	1	1	0	2
No. 32	2	-	0	2
No. 33	-	-	-	0
No. 34	2	1	0	3
No. 35	-	-	-	0

"-" Indicates no information supplied by respondant.

* Calculation checks are defined as a re-working of intermediate calculations, whereas logical checks detect contradictions in the final results.

** The relative weighting inherent in the composite score represents a subjective judgement of importance for the columns.

Certain aspects of data handling not included in Table 3.6, or specifically addressed by the questionnaire, were mentioned by respondants. Direct computer linkage to analytical instruments (for example, Chemex Calgary, Ontario Research Foundation) can reduce opportunities for data transcription errors. Development of computerized performance monitoring for each method based on single operator precision, multiple operator precision and accuracy with standard reference materials was described by the Water Quality Laboratory, and is highly recommended. Monenco discussed retention of raw data used in calculations so that calculations can be rechecked up to two years after analysis. All these procedures contribute to effective quality control and could be used as additional criteria in laboratory evaluation studies.

3.5 Quality Assurance Programs

As with data handling and reporting protocol, quality assurance protocol can be evaluated in a general way, relatively independently of the type of analysis under consideration. An example of this type of evaluation as a first step in laboratory assessment is provided by Josephson (1984). For criteria development purposes, quality assurance was defined in terms of control sample usage and interlaboratory studies. Neither analytical methodology nor documentation of methodology was included under this definition. Quality assurance was evaluated according to professed QA procedures of analytical laboratories (see questionnaire, Appendix 2). Actual effectiveness of quality assurance programs was not assessed.

Laboratories were asked to describe internal quality control addressing use of replicate analyses, spiking, blanks and standard reference materials. Replicates are required for a reliable estimate of precision associated with particular measurements. Blanks are used to quantify background readings as a baseline against which sample readings can be compared. Spiking is used to estimate percent recovery and true chemical concentration by standard addition techniques. Measurements on standards provide an estimate of measurement accuracy. Both precision and accuracy should be quantified with each set of samples processed. The importance and use of control samples for this purpose is discussed by Keith et al. (1984).

External quality control is provided by participation in interlaboratory comparison studies. These studies, usually run by national or international organizations, involve

careful submission of samples for analysis by participating laboratories. Relative standard deviations based on interlaboratory studies are usually higher than those reported by individual laboratories, reflecting differences between labs in methodology, instrumentation or operator performance. Interlaboratory studies permit identification of outlier values and alert the labs producing them to quality control problems that might otherwise not be recognized. A lab rating system based on precision and accuracy in interlaboratory studies is described by Dreesen et al. (1979) with particular reference to uranium mill tailings analysis.

Laboratories were asked to indicate average frequency of involvement in interlaboratory studies as an indication of external verification of their quality control programs. Details of each study were not solicited. It is possible, therefore, that certain parameters measured by a particular lab may not be included in their interlaboratory study program. However, the frequency of studies is probably useful as a general indicator of attention to external verification.

Laboratories were also asked to estimate the percentage of total working time devoted to quality assurance. This percentage may be considered a general indicator of quality control effort. This would include time spent running internal and external quality control samples, and time spent on assessment of method and operator performance.

Table 3.7 summarizes statistics related to quality assurance effort, and provides a possible basis for comparison of responding labs. Each column represents one aspect of quality assurance. Quality assurance time and frequency of interlaboratory studies (columns 1 and 3) were taken from quantitative questionnaire responses. A coding scheme for quantitation of control sample usage was developed a posteriori (see Table 3.7). In cases where a numerical range, rather than a point estimate, was provided, the midpoint of the range is presented in the table. The table represents current laboratory practice and does not necessarily reflect historical quality assurance effort.

Umpire analyses (duplicate samples submitted to an external laboratory) were not considered to have the same value as formal interlaboratory studies. The mine laboratories in Saskatchewan regularly submit high grade ore samples to the Saskatchewan Research Council for confirmation. While this practice does provide an external comparison by which to judge the performance of the mine labs, formal

TABLE 3.7: QUALITY ASSURANCE PROGRAMS

Based on responses provided in the laboratory survey, subject to additional clarification in some cases. Laboratories with and without radionuclide capabilities included.

Laboratory	QA Time	Routine Use of Replicates Standards Blanks	Inter-laboratory Studies	Composite Score**
	% of man-hrs	0 none of above 1 all of above (control sample frequency)	No/year	
No. 1	22.5	1 (.30)	18	3.0
No. 2	10.0	1	17	2.7
No. 3	22.5	1 (.20)	3	2.6
No. 4	12.5	1 (.10)	4.5	2.7
No. 5 •	10.0	1 (.10)	3	2.3
No. 6	10.0	1	1	1.9
No. 7	7.5	1 (.10)	0.5	1.6
No. 8•	20.0	0.5 (.20)	3	2.1
No. 9	8.0	-	10	1.5
No. 10	-	-	-	0
No. 11	-	-	-	0
No. 12	37.5	1 (.54)	18	3.0
No. 13	12.5	1 (.10)	5	2.8
No. 14	10.0	1	6	2.7
No. 15	6.5	1 (.20)	4	2.2
No. 16	5.0	1	3	1.9
No. 17	15.0	1 (.13)	3.5	2.7
No. 18	10.0	1	2	2.1
No. 19	10.0	1	0.5	1.8
No. 20	1.0	0.5	2	1.0
No. 21	15.0	0	1	1.2
No. 22	10.0	1	+1	1.9
No. 23	10.0	1	+1	1.9
No. 24	-	1	+1	1.2
No. 25	-	0.5	4 (?)	1.3
No. 26•	10.0	0	0.1	0.9
No. 28	20	0.5	0	1.5
No. 29	30	1	0	2.0
No. 30	•••	1	3	2.6
No. 31	17.5	1	5	2.0
No. 32	-	1	-	1.0
No. 33	-	-	-	0
No. 34	8	0.5	1	1.7
No. 35	10	0.5	1	1.8

"-" Indicates no information supplied by respondant.
"+" Umpire programs, not considered interlab studies.
• Replicates and standards, but not blanks used routinely.
** The relative weighting inherent in the composite score represents a subjective judgement of equal importance for the columns.
••• Separate QA department responsible for several different labs.

interlaboratory studies have more rigorous controls and numerous participants. The practice as a whole was given the same numerical value (1) as a single formal study, even though it usually involves submission of numerous sample batches. Occasional referee services, provided by some university laboratories, were treated in similar fashion.

Laboratory use of replicates, blanks and standards was quantified in Table 3.7 and expressed as an overall control sample frequency, where possible, on the basis of the questionnaire response. For example, every tenth sample run by the Ontario Research Foundation is a control sample and, on average, every second sample run by the Water Quality Lab is a control. However, laboratories were not specifically asked to provide this frequency.

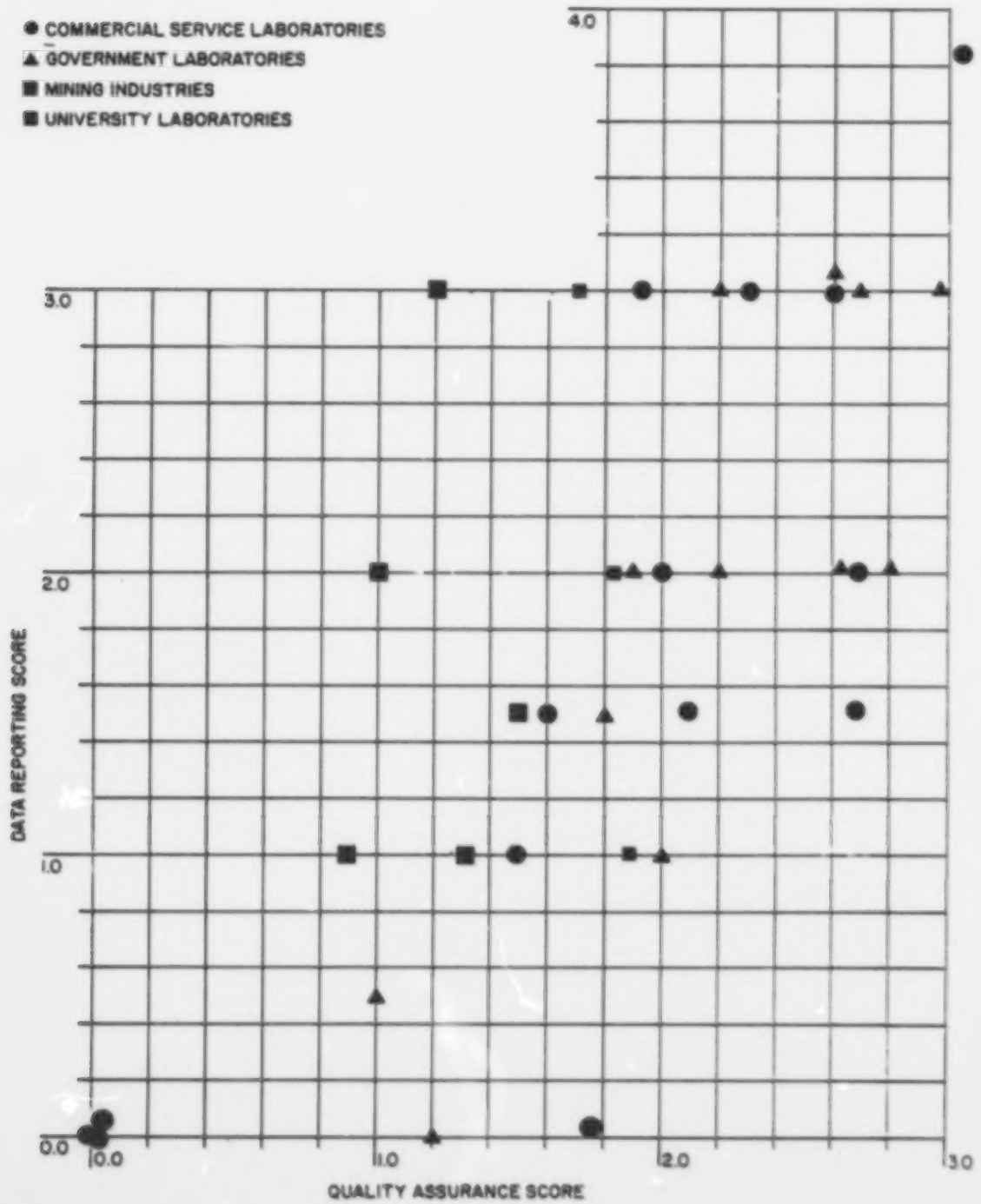
Control sample usage is probably adequate if replicates, blanks and standards are routinely included with each set of samples run. This is indicated in Table 3.7 by a numerical score of 1. Use of some, but not all, of these control sample types on a routine basis is indicated by a fractional score. For example, Beak Analytical Services reports routine use of replicates and standards, while blanks are not included with every set of samples.

For the purpose of comparative evaluation of quality assurance protocol, a composite score is provided in the last column of Table 3.7. This score is calculated as the sum of normalized scores in each of the other columns, and has a maximum value of 3. Normalization of column 1 (QA time) is performed against a maximum of 15%. Thus, percentages greater than or equal to 15 all receive the maximum value (1). Similarly, normalization of column 3 (number of interlaboratory studies) is performed against a maximum of 5/year. This represents a judgement that these are adequate levels of quality control effort. Also, the equal weighting of columns represents a subjective judgement of the relative importance of each factor in ensuring data quality.

Quality assurance scores are roughly correlated with scores for data handling and reporting protocol (Figure 3.1). Both factors can be considered as aspects of quality control. However, other quality assurance criteria, such as overall frequency of control samples in the sample stream, could alter lab scores considerably if incorporated into the evaluation scheme.

FIGURE 3.1

Relationship of Scores for Data Reporting Protocol and Quality Assurance Programs



Quantitative evaluation schemes should be considered no more than approximate and should be verified by independent methods. These methods might include careful examination of laboratory reports for documentation and internal consistency, or blind interlaboratory comparisons.

3.6 Synthesis of Current Laboratory Practices

A synthesis of current laboratory practices is presented below. Detailed responses by each laboratory to the questionnaire are confidential.

Ontario Research Foundation

Ontario Research Foundation, Mississauga, Ontario provides radionuclide analyses for Ra-226, Ra-228, Th-230, Th-232, Rn-220, Rn-222, K-40 and U-235. Analytical methods for the uranium and thorium series are based on the CANMET Report 78-22, "Radiochemical Procedures for Determination of Selected Members of the Uranium and Thorium Series", 1979. The laboratory facilities for gamma counting are fully automated, and alpha counting is partially automated. Internal quality control is regular (about 1 in 10), and 2 to 3 interlaboratory comparisons are conducted every five years or so. Quality control occupies about 5-10% of working time. Most calculations are checked. Formal qualifications of staff range from technical college certificate to Ph.D.

Analytical Chemistry Division, Saskatchewan Research Council

The Analytical Chemistry Division of the Saskatchewan Research Council (SRC), Saskatoon provides analytical services for isotopes from the uranium and thorium series, as well as for most metals. Analytical procedures are well documented and referenced. In addition, Dr. G.L. Smithson of SRC compiled and edited under contract CANMET Report 78-22, "Radiochemical Procedures for Determination of Selected Members of the Uranium and Thorium Series", a comprehensive Canadian reference manual for such procedures. This manual will soon be superceded by a more recent NUTP manual (see Monenco, next page) which updates the SRC compilation. The radiochemical analytical capabilities of SRC include gross alpha, gross beta, Po-210, Ra-226 by two methods, gross alpha and emanation, Ra-228, Rn-222, thorium isotopes (by alpha spectroscopy), Th-232 (both colorimetric and neutron activation), uranium (by four methods, UV fluorescence, colorimetric, delayed neutron counting, and neutron activation analysis).

The SRC laboratories currently provide most of the environmental monitoring of the uranium mining operations in Saskatchewan and participate in more than five on-going interlaboratory quality assurance programs within Canada, on a quarterly to annual basis. Internal quality control checks include blind duplicates, spiked samples, and blanks. Internal quality control constitutes approximately 10% of the analytical workload. All radiochemical procedures are calibrated and checked with NBS traceable standards (some directly from NBS, and others from Amersham). Sample handling procedures (containment, treatment and preservation) conform to EPA and/or Environment Canada protocol. All analytical calculations are checked by the analyst, and results are proofed by his supervisor. All results are stored in a computer which also prints the final report. This report is checked against the worksheet calculations as a final check.

The Analytical Chemistry Division of SRC also analyzes for the following trace metals: bismuth, cadmium, calcium, chromium, cobalt, barium, beryllium, cesium, gold, lithium, molybdenum, rubidium, silicon, strontium, tellurium, tin, titanium, tungsten, vanadium, zirconium, arsenic, selenium, antimony, mercury, boron, sodium and potassium.

Both atomic absorption and plasma emission spectrometry are used. It is hoped that an Argon-Plasma Mass Spectrometer will go into service in 1985.

A further facility for metal (including thorium) analysis is a SLOWPOKE II neutron activation reactor.

Monenco Analytical Laboratories, Calgary

Monenco Analytical Laboratories, Calgary provides analytical services for Ra-223, Ra-214, Ra-226, Th-227, Th-228, Th-230, Th-232, U-234, U-238, Po-210, Ac-227, Pa-231, most gamma emitters, as well as a wide range of metals. Methodology is well documented, based upon "Analytical Methods Manual, National Uranium Tailings Program", by Norman W. Chiu and John R. Dean, Monenco Consultants Ltd., a report prepared for the National Uranium Tailings Program, CANMET, to be published shortly.

Internal quality control contains the following components: publication and distribution of current and complete analytical methods and procedures and analytical instrument

operating instructions; distribution and retention of laboratory reports with provision for administrative technical review; quality control checks on analytical instruments to ensure proper function; a preventive maintenance program; daily calibration of instruments via standards; when available, control samples included with each run (a control sample has a similar matrix and has a working value established by such organizations as ASTM or APHA); when a control sample is not available, a previously run unknown is included as a blind check sample; a reagent blank is analyzed for all parameter determinations; if the results obtained with the standard, control or recycle samples are not within acceptable established limits, the entire batch of analyses is repeated and quality control verified before reports are issued; if sufficiently large samples are not available so as to allow repeat analysis, either the analysis is not accepted by the laboratory, or the client waives evaluation programs. All personnel are trained and qualified in quality control techniques prior to running new analyses. Calculations are carried out by the laboratory supervisor (B.Sc. minimum) and checked by the laboratory manager (Ph.D. level).

Standard reference materials from NBS or comparable standard reference material are used where available, with matrices as close as possible to the unknown samples. About 5% of samples are reference materials, when available; otherwise, previously analyzed and reported samples are substituted for the standard reference material. The laboratory participates in interlaboratory comparisons organized by Environment Canada, Alberta Environment, Saskatchewan Environment, Western Enviro-Agricultural Laboratories Association, USEPA and CANMET.

Non-radionuclides are analyzed as follows: As, Sb, Cr, Hg, Se, Al, Ba, Cd, Cu, Co, Ca, Au, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Si, Ag, Na, Sr, Sn, V, Zn and B.

Atomic absorption and emission spectrometry are available.

Bondar-Clegg and Company Ltd., Ottawa

Bondar-Clegg and Company Ltd., 5420 Canotek Road, Ottawa provide analytical services for radium, uranium, thorium, radon and thoron. The first three are analyzed primarily as total metal. Uranium is analyzed by fluorometry, wet chemistry and neutron activation. No references to analytical methodology are provided. Routine internal

quality control consists of 10% replicates, 5% reference materials and 5% blanks. In special cases, standard addition techniques are used. Comparisons within Bondar-Clegg Laboratories are made on a monthly basis. The Ottawa laboratory participates in the CCIW, CANMET and Radiation Protection Bureau intercomparison programs. About 20-25% of laboratory time is devoted to quality control. The laboratories are well equipped, and a laboratory computer is used. Formal qualifications of staff range from a technology diploma to a Ph.D. Routinely, analytical results are proofread by two persons. Calculations are scrutinized by two persons in addition to the analyst who performed the analysis.

Non-radionuclides are analyzed as follows:

1. Atomic Absorption: cadmium, chromium (acid soluble), cobalt, copper, iron, lead, manganese, molybdenum, nickel, silver, zinc.

2. D.C. Plasma-Atomic Emission: Al, Ca, Fe, Mg, Na, K, Mn, Li, Sr, Be, Ba, Nb, Rb, Ta, Ag, Cd, Cr, Co, Cu, Mn, Mo, Fe, Ni, Zn, V, Bi, As, Se, Pb, Sb, Te, W, U, Sn.

3. X-ray Fluorescence: antimony, barium, bromine, chromium, niobium, rubidium, strontium, thorium, titanium, tin, uranium, vanadium, zirconium, cerium, cesium, gallium, indium, lanthanum, tantalum, yttrium.

4. Neutron Activation: aluminum, barium, bromine, calcium, chlorine, copper, dysprosium, europium, gallium, germanium, indium, iodine, magnesium, manganese, potassium, sodium, strontium, titanium, uranium, vanadium, antimony, arsenic, cadmium, gold, holmium, lanthanum, molybdenum, praseodymium, samarium, scandium, tellurium, hafnium, iridium, iron, lutetium, nickel, rhenium, rubidium, scandium, selenium, silver, tantalum, thorium, thulium, tin, zinc, zirconium, cerium, neodymium, terbium, ytterbium.

IEC Beak Consultants Ltd., Mississauga

IEC Beak Consultants Ltd., Mississauga determine Ra plus a wide range of metals. Methodology is documented in the CCIW Analytical Reference Manual, together with

published papers. Formal qualifications of laboratory staff range from diploma to Master's degree. Internal quality control includes use of replicates, blanks and spiking; interlaboratory comparisons are made two to four times per year on EPA, NBS and NRC reference materials. Quality assurance occupies about 20% of the laboratory time.

Non-radionuclides analyzed include the following: Li, Be, Na, Mg, Al, Si, P, K, Ca, Ti, V, Ca, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sn, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, Ba, La, Hg, Pb, Bi.

Methodology available includes atomic absorption spectrophotometry and DC plasma spectroscopy.

Key Lake Mining Corporation, Saskatoon

Key Lake Mining Corporation, Saskatoon performs analyses for Key Lake's mining operations for Ra-226, uranium, and a variety of metals. Radionuclides are analyzed according to the Eldorado Methods File (internal). Uranium is analyzed by x-ray fluorescence. About 10% of laboratory time is devoted to quality control. The formal qualifications of the staff range from a one to two year technician's course to a bachelor degree. This laboratory is new, having opened in mid-1983.

Non-radionuclides are analyzed as follows:

1. X-ray Fluorescence: U, As, Mo, Ni

2. Direct Current Plasma Spectrometer: Mo, Ni, Fe, Cu, Pb, Zn, Mg, Ca, Ba, Ti, Si, P, K, Na, Zr, B, Mn, Al.

3. Atomic Absorption: As, Se.

4. Wet Chemistry: pH, S.G., EMF, Turb., Spec. Cond., TSS, H_2O, free acid, Fe^{2+}, Fe^{3+}, U (fluor), U (redox), SO_4, Si (grav) (col.), H_2SO_4, SO_2, amine (vol.) (col.) total organic, F, Cl and NH_3 (by select. ion electrode), Cl (vol), coliforms, B.O.D., alkalinity, isodecanol, hexane extractable, alkalinity.

Amok Ltd., Saskatoon

Amok Ltd., Saskatoon perform analytical services for Amok's mining operations, mostly with respect to process control. Uranium is the only radionuclide analyzed in connection with environmental monitoring. All other radionuclides and metals are analyzed by the Saskatchewan Research Council Laboratory. In Amok's laboratories, uranium is analyzed by fluorescence when fused with sodium fluoride, as described in "Manual of Analytical Methods", by J.C. Ingles, Mines Branch, Canada, 1959. The formal education of staff ranges from technical diploma to bachelor degree. Internal quality control consists of the following: duplicate assays; use of a reference standard; sometimes, for special samples with an unknown matrix, use of special addition techniques. Assays are frequently checked against results of the Saskatchewan Research Council.

Wastewater Technology Centre, Canada Centre for Inland Waters

The Wastewater Technology Centre, Canada Centre for Inland Waters, Burlington conducts analyses for Ra-226, Pb-210, Th-230, Th-228, Th-232, gross alpha and gross beta, H-3, C-14, plus a variety of metals. Methodology is documented in the Waste Water Technology Centre Methods Manual (internal). Formal qualifications of laboratory personnel range from a technician with three years college to a bachelor degree. Quality assurance includes use of spikes, standards, blanks. The laboratory participates in EPA round robin intercomparisons for Ra-226 and alpha/beta in water twice per year. Quality assurance occupies about 10% of laboratory time. Data collection and analysis are not computerized.

Non-radionuclides analyzed include the following: Al, Ca, Cd, Cu, Cr, Fe, Ni, Pb, Zn, Mg, Na, K, B, Ba, Au, Co, Mn, Mo, Sn, Sr, Ti and V.

Atomic absorption and argon plasma emission spectroscopy are available.

National Water Research Institute, Canada Centre for Inland Waters

The National Water Research Institute, Radionuclide Section, at Canada Centre for Inland Waters, Burlington, Ontario conducts analyses by well-documented methods. Further, members of the laboratory from time-to-time develop and publish new and/or improved methodology in the refereed open literature. Internal quality control is

practised as follows: check two to three spectra/month, check detector efficiencies with reference samples every three months or so; check background on counters every three months or so. Interlaboratory comparisons (IAEA, USEPA) are made every two or three months. Overall quality assurance occupies 10-15% of total time. The formal qualifications of staff range from high school (with 2 1/2 years university) to Ph.D. and postdoctorals. All data calculations are checked by a supervisor, and all spectroscopy measurements, though computerized, are manually analyzed. The following radionuclides may be analyzed: Pb-210, Cs-137, Ra-226, Th-228, Th-230, Th-232, Pu-240, Pu-239, Am-241, U-234, U-235, U-238, H-3 and Rn-222.

Elliot Lake Laboratory, CANMET

The Elliot Lake Laboratory, Canada Centre for Minerals and Energy Technology, Department of Energy, Mines and Resources, Canada analyzes radioisotopes according to standard methods well-documented in the CANMET Report 78-22, "Radiochemical Procedures for Determination of Selected Members of the Uranium and Thorium Series", 1979. This handbook describes procedures for Pb-210, Po-210, Ra-226, Ra-228, total thorium, Th-228, Th-230 and Th-232. Reference is made to the EML Procedures Manual, edited by John H. Harley, Environmental Measurements Laboratory, 376 Hudson Street, New York, the major repository of standard methods. The laboratory is equipped with modern instruments.

Internal quality control is practised as follows: replicates, blanks, spikes; cross-reference and calibration check every five to ten analyses. Interlaboratory comparisons are made with a frequency of about two to five times per year. Overall quality assurance occupies 10-20% of the work time. Formal qualifications of personnel range from a three-year technologist's training to a Ph.D. Data are checked and proofed by comparison with dummy sample standards and blank samples. No computerization protocol is yet in place.

In addition to radionuclides, metal and non-metal species are analyzed as follows:

Metals: Na, K, Mg, Fe, Ni, Co, Mn, Al, Si, Zn, Ca, Ba, Sr, Pb, Cu, As, Mo, U and Th.

Anions: Cl, Br, F, NO_2, NO_3, SO_3, SO_4 and PO_4.

Physics Department, University of Calgary

The Physics Department of the University of Calgary conducts analyses for radionuclides as part of research programs and, on occasion, for government and industry (50-100 samples per year). Radionuclides measured include the following: all gamma emitters with adequate half-life in the energy range 10 KeV - 5 MeV; alpha emitters including Ra-226, Ra-224, Ra-223, Po-210, Th-230, Th-227, U-238, U-234, U-235, Pa-231; beta emitters via excited gamma emission or bremsstralung; certain metals (e.g., Al, V, Cu) by 14 MeV neutron activation. Chemistry pre-treatment includes KF-pyrosulphate in Pt crucible (U); coprecipitation with $BaSO_4$ (Ra) and purification by chelation; coprecipitation on $Ce(OH)_3$ from chelate at high pH (Th); solvent extraction with tri-iso-octylamine or ion exchange from HNO_3-methanol (U) and electroplating of activity or coprecipitation with CeF_3 after reduction to U IV; coprecipitation with Te (Po); solvent extraction with HDEHP (Ac). A variety of nuclear instrumentation, including a 14 MeV neutron generator, is available. Computer data analysis is used. No technicians are employed.

Quality control of data includes statistical tests on data and inter-calibration of standard sources with other laboratories (NBS, Harwell, Lund-Sweden, CSIRO Australia).

Methods and procedures developed are published in the refereed literature.

Department of Chemistry, Carleton University

The Department of Chemistry, Carleton University performs analyses for Th-230, Ra-226, Th-228, Pb-210, Po-210, Ac-228, Ba-133, Th-224, Fe-59, Pb-214 and Po-218. Most of the methods have been developed in Carleton's laboratories. Most are not yet published. An improved method for the determination of Ra-226 and Th-230 has been published. A variety of counting instrumentation is available. An experienced technician and graduate students are employed. Most analyses are to support internal programs (100-200 Ra or Th per month). Quality control consists of the following: daily background and sensitivity checks; internal consistency checks; if required by client, use of NBS standards. One interlaboratory comparison has been conducted. Data are recorded by hand, which is considered more reliable. All results (not calculations) are checked by the supervisor.

Alberta Environmental Centre, Vegreville

The Alberta Environmental Centre, Alberta Environment, Vegreville, Alberta conducts analyses for Cd, Co,Cu, Mn, Ni, Mo, V, Zn, Cr, Cr (IV), Pb, Al, Be, Ag, Fe, As, Se and Hg. Methodology is documented in the "Methods Manual for Chemical Analysis of Water and Wastes", Alberta Environmental Centre, Alberta Environment. Formal qualifications of staff are as follows:

Technicians - Technical diploma or B.Sc. with six months minimum experience and supervisors - B.Sc./technical diploma with five years minimum experience.

Pre-1981 quality control for metal analysis was as follows:

- every tenth sample run in duplicate to monitor precision;
- every tenth sample spiked with known standard for recovery check;
- internal known check sample run every analytical set;
- internal blind check sample run every two weeks;
- external blind reference samples (EPA, etc.) run minimum four times per year; and
- full participation in interlab studies, usually a minimum of ten samples/year.

Post-1981 quality control for metal analysis practiced as follows:

- calibration confirmation: two internal known independently prepared standards with blank are run daily;
- within run precision: three randomly selected duplicate samples are run daily;
- sensitivity monitor: a low, high and blank standard are run every twenty samples to confirm sensitivity;
- external blind reference samples (EPA) are run a minimum of four times per year or as often as requested by technicians; and
- full participation in interlaboratory studies, usually a minimum of 20 samples per year.

Data are checked by technical and supervisory personnel and are manually entered into a computer for report print-out.

Instrumentation includes an inductively coupled argon plasma emission spectrometer, and atomic absorption spectrometer.

National Hydrology Research Institute, Ottawa

The National Hydrology Research Institute, River Road Laboratories, Ottawa analyze for Ca, Mg, Na, K, Fe, Mn, Zn, Cu, Pb, Hg, Cd, Sr, Si, As, Ba, B and Li. Methodology is documented in Perkin Elmer, ASTM and Standard Methods Manuals. Formal qualifications of laboratory staff range through students on a cooperative course in chemistry or biology, chemical technology graduates, B.Sc. (supervisor), to Ph.D. (laboratory manager). Internal quality control includes the use of replicate analysis, spiking, blanks and reference material, but not in all batchs of samples. Interlaboratory comparisons are made no more than once a year. Overall quality assurance occupies about 10-20% of laboratory working time.

Barringer Magenta, Toronto

Barringer Magenta, Toronto conduct analyses for the following elements: Ag, Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, S, C, Sn, etc., the ions Br^-, Cl^-, F^-, NO_2^-, NO_3^-, PO_x^- and SO_x^-, together with the usual range of water quality parameters (pH, turbidity, various forms of N, hardness, etc.), using methods based on standard procedures (APHA, Environment Canada, EPA, AOAC, ASTM manuals), but with some proprietary modifications. Internal quality control includes use of replicates, spiking, blanks and reference material; about 10% of samples are for internal quality control. The overall quality assurance program occupies about 10-15% of laboratory time. The laboratory participates in "some industry generated, usually government" interlaboratory comparisons. All laboratory reports are proofed, and some or all hand calculations checked. Formal qualifications of technicians range from diploma to bachelor degree, and of supervisors from bachelor degree to Ph.D. Supervisors may perform some analyses.

Major instrumentation includes an inductively coupled argon plasma instrument.

Chemex Labs, Calgary

Chemex Labs (Alberta) Ltd., Calgary conducts analysis for the usual water quality parameters plus a limited range of elements in water samples (Al, Ba, Cr, Cd, Co, Cu, Pb, Li, Mn, Ni, Ag, Sr, V, Zn, Sb, As, Ca, Fe, Mg, Hg, K, Se, Na, Sn, U). In addition, a wide range of elements is analyzed in geochemical samples, as follows (for quantitative analysis): Cu, Mo, Pb, Zn, Ag, Cd, Ni, Co, Fe, Mn, Sb, As, Be, Bi, Cr, F, Au, Hg, Pd, Pt, Se, S, Te, Th, Sn, W, V, Al, Ba, Ca, Li, Mg, K, Rb, Na, Sr, V.

Internal quality assurance programs are practised, and include background correction for matrix effects in atomic absorption. Internal quality control consists of five to seven standards run with every 40 samples; at least one duplicate in each 40 sample set; an annual evaluation of each procedure by running the samples and calculating standard deviations at ten times the detection limit and at mid-range; five samples spiked at two different levels and analyzed for percent recovery; calibration graphs of automated systems compared with previous runs; a system of spike recovery is now being instituted with each set of analysis. Quality control occupies about 20-25% of laboratory time.

Area supervisors are responsible for checking all data, proofing the results and evaluation against internal quality assurance procedures. Many analytical parameters are completely automated and microprocessor controlled. Checks and balances are built into three computer systems which handle data acquisition. Volume of analyses is about 500,000 per year. Nine interlaboratory comparisons are conducted as follows:

U.S. Environmental Protection Agency
Canadian Certified Reference Materials, CANMET
Environment Canada, CCIW, Round Robin
Alberta Oil Sands Program
Agriculture Canada, FICP Program
LRTAP Program, CCIW
Canadian Cooperative Fuel and Lubricant Program, ARC
Western Enviro-Agricultural Lab Association Program
Alberta Department of Environment Pollution Control Program

Formal qualifications of laboratory staff range from diploma to master's degree.

Chemex Labs, Vancouver

Chemex Labs Ltd., Vancouver conduct analyses for the following radionuclides: in water - gross alpha, gross beta, Pb-210, Po-210, K-40, Ra-226, Ra-228, Th-228, Th-230, Th-232, Cs-137 and in solid or vegetation samples - Ra-226, U-238, Th-234, Po-214, Pb-210, Ra-228, Ac-228, Th-228, Ra-224, Rn-220, Po-216. In addition, geological analyses are conducted for most elements in the Periodic Table, using a variety of techniques including atomic absorption spectroscopy, inductively coupled plasma spectroscopy and neutron activation.

Geoscience Laboratories, Ontario Geological Survey

The Geoscience Laboratories, Ontario Geological Survey, Toronto conduct analyses for elements as follows: Li, Be, Na, Mg, Al, K, Ti, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cr, Rb, Sr, Y, Zr, Nb, Mo, Ra, Rn, Pd, Ag, Cd, Sn, Sb, Cs, Be, La, W, Pt, Au, Hg, Pb, Bi, Ce, Nd, Sm, Eu, Cd, Dy, Yb, Th, U. Methodology is documented in the Geoscience Laboratories Manual, an internal manual open to inspection. Internal quality control is by use of an extensive open end blind program of duplicates, triplicates, replicates, in-house standard reference materials and internal standards. Internal quality control accounts for about 10% of samples. Interlaboratory comparisons are conducted in an international working group on geostandards, contract work and local "round-robins" to the extent of about ten per year. Data are checked in two stages by the supervisor and chief analyst, and stored on a database as a "historic" record. Formal educational qualifications of laboratory staff range from no "formal" qualifications (Tech. 3 (Chem Lab)) to a Ph.D. Volume of analysis is about 150,000 per year.

Instrumentation includes atomic absorption, x-ray fluorescence and inductively coupled plasma spectroscopy.

Alberta Research Council, Edmonton

The Alberta Research Council, Edmonton carries out analyses for heavy metals and conventional water quality parameters. Metal analyses are performed by atomic

absorption spectrophotometry and inductively coupled plasma spectroscopy. Internal quality control consists of replicate analyses, spiking, use of reference materials, blanks, standard addition and frequent recalibration. There is no formal schedule of interlaboratory comparisons, but the laboratory participates in CANMET intercomparisons. Quality control occupies about 10% of working time. Qualifications of laboratory staff range from diploma to B.Sc., to Ph.D. for the supervisor. Data are proofed and calculations spot-checked.

Nova Scotia Research Foundation

The Nova Scotia Research Foundtion conducts analyses for water samples and metals. Analytical facilities include atomic absorption and x-ray fluorescence and diffraction. Formal qualifications of personnel range from technical school graduate to Ph.D.

Water Quality Laboratory, Canada Centre for Inland Waters

The Water Quality Laboratory, Canada Centre for Inland Waters, Burlington conducts analysis for a wide range of non-radionuclide water quality parameters, including many metals, as outlined in the Analytical Methods Manual, 1979, Inland Waters Directorate, Water Quality Branch, Ottawa. Extensive instrumentation is available, including atomic absorption, atomic emission and inductively coupled plasma emission spectroscopy for metal analyses. All methodology is well-documented in the manual cited above. Internal quality control includes the use of standards, blanks, duplicates, spikes and dilutions. Quality control analyses contributed about 54% (116,000) of the total in the last fiscal year. Nine discrete interlaboratory comparison programs vary in frequency from monthly to annually, depending on programs. Overall, quality assurance amounts to about 35-40% of total laboratory working time. Data reporting protocol includes computerization, calculation checking and a multi-stage review process.

Institute of Environmental Studies, University of Toronto

The Institute of Environmental Studies, University of Toronto conducts metal analyses on inductively coupled emission plasma spectrometer, atomic absorption spectrophotometer, and the University's Slowpoke neutron irradiation reactor. Analyses for Pb-210 and Ra-226 are conducted in the Department of Chemistry, University of Waterloo following

pre-concentration on ion exchange resin. Sample preparation and analytical procedures are documented. Every set of samples is analyzed together with an NBS standard. Interlaboratory comparisons are not made regularly. Data collected are checked for impossible or improbable numbers and for conditions that are mutually exclusive. In a few instances, the same element is analyzed by different methods. For each laboratory analytical method, staff qualifications range from Ph.D. (supervisor) to bachelors degree. Non-radionuclides analyzed include Pb, Ni, Cu, Co, U, Ba, Mg, V, Al, Mn, Ca, As, Cd, Fe, Zn, Th, Si.

Lakefield Research, Lakefield

Lakefield Research, a Division of Falconbridge Ltd., Lakefield, Ontario conducts analyses for uranium and thorium, as well as a wide range of heavy metals. About 80-100,000 analyses are conducted per year. Quality assurance programs occupy about 8% of the laboratory working time. About ten interlaboratory comparisons are made each year. Data are initially recorded in paged workbooks; all assays are controlled by the supervisor. Formal qualifications of laboratory staff range through bachelor degree to Ph.D.

Mineral Sciences Laboratory, CANMET, Ottawa

The Chemical Laboratory, Mineral Sciences Laboratory, CANMET, Ottawa conducts analyses for the following nuclides: Ra-226, Th-230, Pb-210, U and Th. Analysis of the first three of these is based on CANMET Report 78-22, but there are many important changes which are not yet fully documented. Uranium determination is usually by fluorometry, but uranium and thorium (as well as yttrium and iron) in organic solution are analyzed by x-ray fluorescence.

In addition to the above nuclides, the laboratory analyses for practically all of the elements of the periodic table, using a wide variety of techniques including atomic adsorption, x-ray fluorescence, neutron activation, and ICP. The volume of analyses for the year 1982/83 was 45,000.

Quality assurance is practised through use of certified reference materials, previously analyzed samples, and/or prepared synthetic samples. Internal quality control includes

use of replicates, spiked samples, blends, reference material. Reference procedures are often used especially when testing procedures to establish validity, spiking, blanks, and replicate analyses are used routinely. Work books including calculations are usually checked by the supervisor who verifies the results reported. Analysis results are reported by computerization, but may be reported verbally or otherwise on request. More than 5% of laboratory time is spent in quality control.

Atomic Energy Control Board Laboratories

The Atomic Energy Control Board conducts analysis for the following radionuclides: H-3, C-14, Ni-63, Co-60, Cs-137, Ba-133, Ir-192, P-32, S-35, Cl-36, K-40, Cr-51, Fe-55, Fe-59, Sr-89, Sr-90, I-125, I-129, Po-210, Bi-210, Pb-210, Ra-223, Ra-224, Ra-226, Th-232, U-238, Rn-222, Po-218, Pb-214, Bi-214, Po-214, etc., gross beta and gross gamma. The methodologies used are documented in CANMET Report 78-22, "Radiochemical Procedures for Determination of Selected Members of the Uranium and Thorium Series", June 1979, the HASL Procedures Manual, Report HASL-300, U.S. National Technical Information Service, 1972, and various published reports, especially those of C.W.Sill in Anal. Chem. Formal qualifications for laboratory personnel range from a community college to a university degree. Internal quality control includes daily counting checks and use of standard reference materials and blanks. Interlaboratory comparisons are made every six months on Rn-222, and infrequently and irregularly or often. Currently, quality assurance occupies 1% of laboratory time. A quality assurance program is currently being developed. Computerization of data handling is also currently being developed.

In addition to radionuclides, the following non-radionuclides are analyzed: arsenic, cadmium, lead, mercury, sodium, potassium, calcium, magnesium, barium, cobalt, copper, iron, manganese, uranium, zinc, beryllium, cesium, iridium, molybdenum, nickel, niobium, phosphorus, thallium, strontium, vanadium, yttrium, zirconium, silver, ammonia, chloride, fluoride, hardness, hydrogen sulphide, inorganic phosphate, nitrate, nitrite, sulphate, sulphite, carbonate, bromide, iodide.

Major instrumentation includes atomic absorption, x-ray fluorescence and x-ray spectroscopy.

Enviroclean

Enviroclean, a division of MacLaren Plansearch Inc., London, Ontario conducts analyses for a wide range of trace metals and elements. Instrumentation includes an atomic absorption spectrophotometer, a hydride generator for arsenic, selenium and antimony, a cold vapour mercury analyzer and an autoanalyzer. Methods are drawn from recognized sources whenever possible. Internal quality control includes duplicates, blanks and spikes or standards with every set of samples. Participation in interlaboratory studies includes Environment Canada (FPCAP), International Joint Commission, Agriculture Canada (FICP) and Consumer and Corporate Affairs (UFFI) programs. Permanent staff qualifications range from wide technical experience in lieu of formal credentials, to M.Sc. and Ph.D.

Acres Chemistry Laboratory

Acres Chemistry Laboratory, Acres Consulting Services Ltd., Niagara Falls, Ontario conducts analysis for all common metals. Methods generally follow the Analytical Methods Manual, 1979, Inland Waters Directorate, Water Quality Branch, Ottawa. Instrumentation includes atomic absorption and an autoanalyzer system. Internal quality control is modified from EPA-600/4-79-019, a document which provides for regular use of replicates, spikes, blanks and standards, control charts and performance audit. Interlaboratory studies are performed as required. Data storage and reporting are computerized. Staff qualifications range from chemical technologist to Ph.D.

Atomic Energy of Canada Ltd.

Atomic Energy of Canada Ltd., Chalk River Nuclear Laboratories, Chalk River, Ontario offer a complete range of environmental services, including analytical chemistry, geochemistry and radiochemistry. Standard analytical instrumentation includes ion chromatography and flame or graphite furnace atomic absorption spectrophotometry. Radiochemical instrumentation includes high resolution gamma ray spectrometry, alpha spectrometry, gross alpha and beta counting and liquid scintillation counting. Experience includes H-3, C-14 and Rn-222 analysis and U and Th radiochemistry in water, soil and vegetation.

University of Alberta

The Environmental Engineering Laboratory, Department of Civil Engineering, University of Alberta, Edmonton has capabilities for analysis of Ra-226 in aqueous samples and in (Ba, Ra) SO_4 precipitates. Methods, based on de-emanation of Rn-222, are well documented with published references and complete description of protocol. Standards from NBS are used for calibration. All samples for Ra-226 analysis are acidified with 2% HNO_3 by volume. Samples to be analyzed for dissolved Ra-226 are passed through a 0.45 um filter prior to acidification. A minimum ingrowth time of six days is allowed, with most samples averaging seven to ten days. Although the laboratory is not involved in exchange programs for Ra-226 determination, it has participated in the NUTP program by analysis of three standards. Replicates are routinely analyzed with every experiment. Several blanks have also been prepared and analyzed. Formal qualifications of analyst and supervisor are B.Sc. and Ph.D., respectively.

Northern Forest Research Centre, CFS

From 1981 to 1985, the Northern Forest Research Centre, Canadian Forestry Service, Environment Canada, Edmonton, Alberta operated a Radiochemistry Analytical Laboratory in support of environmental research on radionuclides in forest vegetation and soils. The lab is still in existence, but is not currently staffed. In 1984, its radionuclide capabilities included Ra-226, Rn-222, Th-232, Th-230, Rn-220, Po-210, Pb-210, U-235, U-234, natural U, Ba-133 and gross α, β and γ. Metal parameters included 26 elements by ICP and more than 30 elements by neutron activation analysis using the University of Alberta Slowpoke reactor. Basic analytical references included CANMET Report 78-22, the Eldorado Procedures Manual (unpublished), the HASL Procedures Manual, several publications by C.W. Sill and the U of A Slowpoke Facility Annual Reports, 1977-84. Modifications to these methods are described in detail. Available instrumentation includes an Rn detector and Rn bubbling system, an α, β, γ counter, several multichannel analyzers, an spectrometer with surface barrier, NaI, ZnS and Ge(Li) detectors, and a delayed neutron counting system. Internal quality control included triplicate analysis on every third sample, four spiked samples per batch of 20, and four blanks per sample batch. The laboratory has not yet participated in interlaboratory programs. Overall quality assurance occupies approximately 30% of working time in 1984. Staff qualifications ranged from the undergraduate student level to Ph.D. Data storage and reporting are computerized.

Ontario Ministry of the Environment, ITC

The Inorganic Trace Contaminants Section of the Laboratory Services Branch of the Ontario Ministry of the Environment has analytical capabilities for a wide range of metal and nutrient parameters. In the Cardiff Radiological Program, these have included As, U, Al, Cd, Co, Cr, Cu, Ni, Pb and Zn. Arsenic is determined by hydride-atomic absorption spectrophotometry and U by a fluorometric procedure. Other metals are determined either by atomic absorption or inductively coupled plasma emission spectrometry. Methodology is documented in an internal Handbook of Analytical Methods for Environmental Samples, Laboratory Services and Applied Research Branch, Ontario Ministry of the Environment, Vol. I, December 1983. Quality assurance is administered by a quality control officer responsible for the ITC and other ministry laboratories. Internal quality control includes analyses of within- and between-run duplicates (at least 1 in 20 samples), spikes, blanks (every run) and reference materials (2 per run). External quality control includes participation in interlaboratory comparisons organized by the Canada Centre for Inland Waters (LRTAP study), the International Joint Commission (IJC), and Fisheries and Oceans Canada. Sampling is conducted by trained environmental officers following the Ministry's Guide to the Collection and Submission of Samples for Laboratory Analysis, 1979. Data handling and reporting is fully computerized under the control of a central Laboratory Information System. Formal qualifications of technicians range from community college to B.Sc., while scientists are qualified at the B.Sc. to Ph.D. level.

Freshwater Institute

The Freshwater Institute, Winnipeg, Manitoba conducts analyses for U and Th series radionuclides, Be-7, Cs-137 and all γ metal isotopes. Analytical methods and quality assurance procedures are currently in press in the form of a methods manual. Instrumentation includes a number of α spectrometers, Ge(Li) detectors, multichannel analyzers and α scintillation counters. The institute has participated in the CANMET reference materials program (Smith and Steger, 1983) as part of its external quality control. Data handling and reporting are computerized. Laboratory staff are qualified at the B.Sc. level.

Rio Algom

Rio Algom Limited, Elliot Lake, Ontario conducts analyses for U (x-ray, fluorometric, colorimetric, gravimetric), Th (x-ray, radiometric, colorimetric, gravimetric) and Ra-226 (alpha-scintillation following radon de-emanation) in addition to 38 metals and other elements by atomic absorption flame spectroscopy, and other physical-chemical analyses. Instrumentation includes atomic absorption analysers, x-ray analysers, spectrophotometers, scintillation counters, an emission spectrograph and a fluorimeter. Methods are referenced to equipment manuals, standard methods manuals (ASTM, APHA), government laboratory manuals including Ingles (1958), and periodicals. Minor modifications are described. Sixty percent of analytical staff have 25-30 years experience, 30% hold relevant degrees, and 50% have completed specialized training courses. The lab performs 4,000-5,000 determinations per month. Quality assurance includes routine use of standards and blanks, duplicates for custom assays, and participation in exchange and umpire programs. About 5-10% of lab time is devoted to QA. Data reporting protocol includes double proofing and routine calculation checks.

Radiation Protection Bureau

The Radiation Protection Bureau, Health Protection Branch, Health and Welfare Canada, was established in 1960 and conducts analyses for U, Th, Po-210, Pb-210, Ra-226 and Rn-222, all gamma emitters, Sr-89, Sr-90, Cs-137, Ba-140, I-131, H-3, calcium and potassium in a variety of matrices. Instrumentation includes a wide variety of counters, detectors, multichannel analysers, alpha and germanium spectrometers, fluorometers, dosimeters and TLD readers. About 3,000-4,000 analyses are performed per year. Uranium is determined fluorometrically, Ra-226 by co-precipitation and counting of Bi-210 emission, and Po-210 by acid extraction into isopropyl ether, stripping and alpha counting.

Water Laboratory, Department of Indian and Northern Affairs

The DIAND Water Laboratory in Yellowknife, NWT, conducts analyses for arsenic, cadmium, copper, iron, lead, mercury, nickel, zinc and chromium, among other water quality parameters. Methods follow APHA Standard Methods with no significant deviations. Instrumentation includes both flame and furnace atomic absorption spectrophotometry. Staff include university and technical school graduates. About 3,000

analyes per year are performed. Quality assurance includes blanks and standards with every batch of samples and interlaboratory studies once per year, and occupies about 10% of staff time.

4.0 CRITERIA DEVELOPMENT AND SYNTHESIS

4.1 Definition of Ideal Data Set

An ideal data set would have associated with it a formal quality control program, and sufficient documentation that the user could make independent judgements concerning data quality, based on methodology and quality control. While it does not seem feasible to incorporate such detailed documentation into a database directly, it should be possible for potential users to obtain such information. Therefore, the laboratory which performed each analysis should be identified.

Similarly, the organizations or individuals responsible for sampling and field measurements should be identified since data quality depends on correct sampling and measurement procedures in addition to careful chemical analysis. Sampling is seldom the responsibility of the analytical laboratory.

Samples should be collected by professional or trained technical staff. Documentation of sample collection and handling should include sample type, location, depth and field conditions, methods of collection, preservation, filtration and storage, and description of any measurements or analyses performed in the field.

Samples and field measurements should form part of a continuous sampling and monitoring program, with repeated samples and measurements at the same location. This enables database users to develop realistic probability density functions for stochastic modelling purposes, and increases the usefulness of the data.

The ideal data set will have been generated by a reputable laboratory which is highly rated for its methodology (documentation and performance), data reporting protocol and quality assurance program. Suggested rating schemes are presented in Tables 3.5, 3.6 and 3.7.

Methodology should ideally be documented in external publications. Laboratory involvement in methods development, strong staff credentials and demonstrated consistent performance in interlaboratory comparisons all increase confidence in the application and choice of methodology.

Data reports should be proof-read thoroughly, and calculations checked prior to release. Records should ideally be stored on a computerized system, which performs logical data checks and method performance evaluations. Computerization facilitates this type of evaluation when large volumes of data must be handled.

The quality assurance program should be formalized and well-documented. Control samples, including replicates, standards and blanks, should be used routinely, and should accompany every set of samples analyzed. Laboratories should be included in regular interlaboratory comparisons, and should devote a substantial percentage of working time to quality control.

4.2 Nature of Data in the CANUT Database

The CANUT database was structured to allow for a quality factor to be associated with each measurement. However, available documentation in support of individual measurements does not permit derivation of quality factors for individual measurements. Quality ratings for whole blocks of data, based on general procedures and performance of the analytical labs involved, would be more appropriate.

The source code associated with each measurement in the database could be used as a basis for grouping the data into blocks. Each block of data could then be assigned a quality factor, according to its source. This approach assumes that source codes can be associated with particular analytical laboratories.

Certain data sources, such as the Ontario Ministry of Environment, are easily associated with an analytical laboratory. Inorganic chemistry is performed by the MOE in-house (Inorganic Trace Contaminants Laboratory), and radiochemical analyses are conducted by the Ontario Ministry of Labour (Radiation Protection Laboratory).

Other data sources, as designated in the CANUT database, are associated with many different analytical laboratories, and the associations change with time. The NAQUADAT data from Water Quality Branch, for example, may represent chemical analysis performed at any one of three (3) federal laboratories, or numerous regional laboratories, depending on the time period. Similarly, ESQUADAT data from Saskatchewan Environment includes chemical analyses performed at any one of four (4)

different laboratories, depending on the time period, the mining company responsible and the parameter measured (Table 3.2). In these cases, data blocks should be defined to correspond with analytical laboratories, rather than with source codes as currently used to identify data sources.

Source codes cannot easily be associated with information on general sampling procedure. Sampling procedure tends to be poorly documented. Most analytical laboratories report appropriate sample collection and preservation techniques when directly involved in the sampling program. However, most laboratories also report that they are seldom directly involved.

The organization responsible for sampling has been identified for most of the data in the database, and can usually be associated with the source code. In the case of the Ontario Ministry of Environment's Bancroft and Cardiff radiological studies, MOE regional staff were responsible for sampling. NAQUADAT data are generally based on samples collected by Water Quality Branch staff. However, samples contributing to Saskatchewan Environment's ESQUADAT database are generally collected by the mining companies. Mine sampling techniques tend to be process-oriented, and may not comply with environmental sampling standards.

4.3 Framework for Criteria Development and Rationale

A number of possible criteria for development of quality factors have been presented (Tables 3.5, 3.6, 3.7), based on documentation of analytical methodology, staff qualifications, laboratory performance, data handling and quality assurance protocol. Criteria based on sample collection methods have been devised but have not been illustrated due to a paucity of information on sampling techniques employed by contributors to the CANUT database.

The criteria considered may not be of equal importance to all users of the database. Certainly, the laboratories involved would disagree on the relative importance of some criteria. University laboratories, for example, play an important role in methods development and document their methods in the open literature. This could be considered their primary function. Yet their sample load is usually not sufficient to justify a formal quality control program. Multiple criteria would portray the strengths

and weaknesses, permitting the user to weigh them, whereas an average overall score would not.

For most applications, the user would opt for quality control in selecting data for a model. However, for models of chemical processes in difficult matrices where standard methods have not worked well, methodological expertise may be preferred.

Multiple criteria would convey more information to the user, but would require a greater degree of user interpretation. A small number of criteria, reflecting conceptually different aspects of data quality, is probably optimal.

Interpretive effort can be minimized by use of a simple quality scale. A discrete variable with few character states should be adequate.

Since data reporting protocol and quality assurance are conceptually similar aspects of quality control, they could be combined as a single composite criterion (Tables 3.6 and 3.7). Documentation of analytical methodology, staff qualifications and laboratory performance (Table 3.5) should probably be treated together as an additional composite criterion.

Sampling methods associated with existing CANUT data are not well documented and would therefore receive a low quality rating. However, ratings based on sampling continuity may be much better. Such criteria could be defined in terms of data requirements for particular applications.

The process of selecting and quantifying criteria for evaluation of data quality is necessarily based on certain value judgements. In recognition of this subjective component, quality factors incorporated into a database should be considered approximate rather than absolute.

Application of quality factors should be restricted to the framework within which they were developed. This would preclude rating of historical data quality according to the generating laboratory as assessed by its current practices. Similar considerations require that criteria based on assessment of laboratory practices be updated periodically in order to reflect any changes in protocol.

4.4 Preliminary Recommendations

A list of required criteria for evaluation of data quality is presented in Table 4.1. Components of each criterion are briefly described in general terms. Possible quantification systems are introduced in Section 3 and revised and tested in Section 5. Recommendations on implementation of criteria are as follows:

1. A multiple (4) criteria system for designation of data quality is recommended.

2. One criterion, applied according to the identity of the analytical laboratory, should reflect various aspects of quality control, including data reporting protocol and quality assurance programs.

3. Other laboratory-specific criteria might include documentation of analytical methodology and/or consistency of performance.

4. A criterion representing the continuity of the sampling and field measurement program (i.e., amount of data in relation to needs) can be defined on a project specific basis.

5. Other sampling criteria addressing documentation of sampling and handling methods and personnel should be considered, in conjunction with improvements in sampling documentation for newly acquired CANUT data.

6. All criteria should be quantified on a simple numeric or alphabetic scale.

7. Draft criteria based on laboratory protocol should be presented to participating laboratories with an opportunity to comment and provide additional relevant information.

8. Information relevant to final criteria should be obtained and filed for all future database entries.

9. Proposed laboratory-specific criteria should not be applied to data generated prior to 1980, since adequate documentation of protocol does not encompass more than a five-year period at most laboratories.

10. Criteria should be reviewed at frequent (5-10 year) intervals in order to re-assess relevant laboratory protocol.

TABLE 4.1: REQUIRED COMPONENTS OF CRITERIA FOR EVALUATION DATA QUALITY

Criterion	Components
Quality Control[1]	quality assurance program data reporting protocol
Analytical Documentation[1] and Performance	documentation of methodology staff qualifications performance on interlaboratory studies
Sampling and Handling	documentation of methods and field conditions staff qualifications chain of custody
Continuity of the Sampling Program[2]	amount of data available by region

[1] Laboratory-specific criteria applied to blocks of data according to the generating laboratory.

[2] The last criterion represents data quantity rather than quality, however, data quantity can limit the quality of a predictive modelling effort. The amount of data required and the definition of a region of interest must be project specific.

5.0 REVIEW AND APPLICATION OF CRITERIA

The objective of Phase II studies were as follows:

1. To verify the feasibility of applying the recommended criteria by deriving quality factors for a variety of data sets.

2. To verify that these quality factors based on proposed criteria correspond with other independent measures of data quality.

Independent measures of data quality may include:

2a. Overall assessment of written reports from which certain sets of data have been derived.

2b. Assessment of internal consistency (contradictory values, etc.) of data in blocks which have been assigned quality factors.

The latter approach was used in the present study, although written reports when available were utilized in defining homogeneous data sets and identifying appropriate tests of internal consistency.

5.1 Peer Review and Revision of Criteria

Preliminary criteria for subjective evaluation of data quality were developed in Sections 3 and 4. These criteria were designed to assess characteristics of the sampling program and analytical laboratories associated with a particular data set, rather than actual properties of the data. In order to arrive at a final set of subjective criteria that would likely reflect real data properties, the criteria and the quantitative scoring system based on the criteria were subjected to an extensive peer review process in several stages.

The first stage of the peer review process consisted of internal review by NUTP and CANMET staff and advisors. Based on these reviews, the criteria and the point scoring system were revised so as to reflect a concensus within that group as to which criteria

were most likely to reflect real data quality. The revised criteria at this stage are included in Appendix 3.

In order to achieve a broader concensus, the revised criteria were distributed for comment to a large number of analytical laboratories, including all laboratories which had initially supplied information on analytical and quality assurance protocol (Table 3.3), many laboratories which had not initially participated, and a variety of environmental consultants and government agencies with environmental sampling expertise. Table 5.1 lists the affiliations of all individuals invited to comment as external reviewers. Out of 51 potential respondants, 22 replied with constructive comments, suggestions and opinions concerning the relative weighting of criteria inherent in the scoring system. All replies are included in Appendix 4.

Several points of concensus emerged from the peer review process, as follows:

1. The point spread between external and internal documentation of methods was too great. Intermediate categories were suggested. Minor modifications to published methods are widely used and, if validated on control samples (standards, spiked samples and blanks), should not be strongly penalized.
2. Education is only one, and perhaps not the most important, documentation of staff credentials. Experience should be considered a valid credential.
3. Weighting of interlaboratory performance should be increased since this is the only criterion approaching a direct measure of laboratory quality.
4. More specific indications of the type of information which constitutes adequate sampling documentation are required.

There was general agreement that the criteria should be verified by examination of relationships to independent objective measures of data quality. However, there were concerns regarding the accuracy of information supplied by laboratories and samplers in support of the subjective laboratory scores. There was also a concern that the proportion of analytical or sampling errors, which result in logical inconsistencies that can be objectively identified as errors, may be small.

Some concerns were expressed regarding the application of a subjective quality score. In particular, it was emphasized that such scores should not be used to eliminate data from

TABLE 5.1: REVIEWERS INVITED TO COMMENT ON PROPOSED CRITERIA FOR DATA QUALITY EVALUATION

Acres	Monenco
Alberta Environmental Centre	Monserco Labs
Amok Ltd.	National Hydrology Research Institute
Atomic Energy of Canada	National Research Council
Atomic Energy Control Board	National Water Research Institute
Barringer-Magenta	Noranda
Bondar-Clegg	Nova Scotia Research Foundation
B.C. Research	Ontario Geological Survey
Canadian Forestry Service	Ontario Ministry of Environment
Canmet (Elliot Lake, Ottawa)	Ontario Research Foundation
Carleton University	Radiation Protection Bureau
Chemex (Calgary, Vancouver)	Radiation Protection Lab
Correlation Labs	Rio Algom
Denison Mines	Saskatchewan Environment
Dept. of Indian and Northern Affairs	Sask. Mines Pollution Control Branch
Dillon Consultants	Saskatchewan Mining & Development Corp.
DSMA Atcon Ltd.	Saskatchewan Research Council
Eldorado, Ottawa	Senes Consultants
Enviroclean (MacLarens)	University of Alberta
EPS, Ottawa	University of Calgary
Esso Resources	University of Toronto
Freshwater Institute	University of Waterloo
Geological Survey of Canada	Wastewater Technology Centre
Golder Associates	Water Quality Lab
Key Lake Mines	X-ray Labs
Lakefield Research	

a data base, but rather to flag the data as suspect. For some applications, data quality requirements may be much more stringent than others, and decisions to use or not use a particular block of data should be made a posteriori with the application in mind.

Several new criterion components were introduced at the suggestion of reviewers. A component of the quality control criterion was added, reflecting protocol for reporting of determinations which are less than the method detection limits. The various protocols used and their relative merits are discussed by Keith et al. (1983) and Miedema (1983). Also, a component of the sampling criterion reflecting collection of replicate samples was added. Replicate samples can be used as a check on the consistency of sampling technique.

The final set of proposed criteria for data quality evaluation based on laboratory and sampling protocol are presented in Table 5.2. These criteria are considered to reflect a broad concensus among the scientific community.

5.2 Verification of Criteria for Data Base Evaluation

The revised criteria in Table 5.2 are the result of an extensive peer review and revision process. Consequently, they may be taken to represent a concensus among the scientific community, insofar as concensus among this community is possible. However, concensus as to the best way of evaluating a set of data without access to specific methodological and quality control information associated with the data set, does not necessarily imply that such an evaluation process is meaningful. A number of reviewers have expressed reservations concerning the relationship between any general laboratory evaluation criterion and actual data quality (Appendix 4). All have concurred that this relationship should be investigated in order to verify the utility of such criteria, prior to application.

Evaluation criteria based on general laboratory protocol must be considered subjective since they are not derived from an analysis of the actual data produced by the laboratory. Objective evaluation criteria can be defined in terms of expected relationships between different parameters included in the data set. These relationships form the basis of the "logical checks" referred to in the subjective evaluation system (Table 5.2) as a positive aspect of quality assurance protocol. Agreement between subjective and objective quality scores for a particular data set can be used to verify the utility of the subjective evaluation system.

TABLE 5.2: PROPOSED CRITERIA FOR DATA QUALITY EVALUATION

CRITERION REPRESENTING ANALYTICAL METHODOLOGY

Component		Points
A.	All methods used for reported results, at least:	
	externally documented (peer reviewed and published), unmodified	10
	OR	
	referenced to external publication, modifications validated	8
	OR	
	referenced, modifications not validated but open to inspection	6
	OR	
	internal, validated with standards and appropriate matrix	4
	OR	
	internal, not validated but open to inspection	2
	OR	
	internal or referenced with modifications, not validated or open to inspection	0
B.	Lab involved in developing (and validating) <u>new</u> methods	3
	OR	
	Not involved in methods development	0
C.	Highest level of education or experience:	
	relevant Ph.D. or 15 years	3
	OR	
	relevant M.Sc. or 10 years	2
	OR	
	relevant B.Sc./Technical Diploma or 5 years	1

D. Successful* performance in recent widely recognized** inter-laboratory comparison (degree of internal precision, relative to other participants) 5-10

OR

Successful* participation in other formal interlaboratory exchange study or umpire program 5

OR

No comparison with other labs or poor performance 0

Composite point score (A-D) = sum of points, normalized against the maximum possible and converted to a 0-9 scale.

* Average or better precision and within statistical limits of study.

** Summary data published or available from sponsor of study.

CRITERION REPRESENTING ANALYTICAL QUALITY CONTROL

Component		Points
A.	Report proofing for transcription errors:	
	double	5
	single	3
	none	0
B.	Checking (i.e., reworking) intermediate calculations:	
	all calculations checked	5
	spot checking with all calculations computerized	5
	spot checking	3
	no checking	0
C.	Logical checks by computation (e.g., statistical outliers, control charting, mass balance and ion balance:	
	all above performed in all applicable cases	10
	all performed in some cases	8
	some performed, all cases	6
	some performed, some cases	4
	not performed	0
D.	Time devoted to quality assurance (% of total man-hours, normalized against a maximum of 15%, i.e., percentages ≥ 15 result in the highest score of 15)	0-15
E.	Routine use of within and between run duplicates, standards spiked samples and blanks:	
	all above used routinely (every batch of samples)	10
	some of above used routinely	5
	none of above used routinely	0
F.	Number of relevant interlaboratory studies per year (normalized against a maximum of five studies per year, i.e., frequencies ≥ 5 result in the highest score of 10)	0-10
	OR	
	Routine submission of duplicates to another reputable lab (entire "umpire" program considered equal to a single formal interlaboratory study)	2
G.	Measurements less than detection limit reported as:	
	a value $\pm$ analytical error	5
	OR	

less than detection (detection limit stated and defined)	4
OR	
less than detection (detection limit not stated and defined)	3
OR	
a value equal to detection limit	0
OR	
zero	0

Composite point score (A-G) = sum of points, normalized against the maximum possible and converted to a 0-9 scale.

CRITERION REPRESENTING SAMPLING METHODOLOGY

Component		Points
Sample Collection and Identification		
A. Sample type (phase, matrix, colour, turbidity):		
Documentation adequate		1
Documentation inadequate		0
B. Location (position, depth):		
Documentation adequate		1
Documentation inadequate		0
C. Collection methods (equipment, calibration, flushing):		
Documentation adequate		1
Documentation inadequate		0
D. Chain of sample custody (individual responsible, sample number, name of collector, date of collection, shipping, receiving):		
Documentation adequate		1
Documentation inadequate		0
E. Sampling staff qualifications or experience:		
Technical or professional or 5 years		1
No formal credentials		0
Not stated		0
F. Collection of replicate samples:	≥ 10%	5
	≥ 1%	2
	< 1%	0
Treatment Methods		
G. Sample preservation (acidification, refrigeration):		
Documentation adequate		1
Documentation inadequate		0
Procedure not appropriate*		1
H. Sample filtering (pore size):		
Documentation adequate		1
Documentation inadequate		0
Procedure not appropriate*		1

I. Sample storage (time, conditions):

Documentation adequate	1
Documentation inadequate	0

Field Analysis (instrumentation, calibration, equilibration):

J.	pH, Eh:	Documentation adequate	1
		Documentation inadequate	0
		Procedure not appropriate*	1
K.	Specific conductivity:	Documentation adequate	1
		Documentation inadequate	0
L.	Temperature:	Documentation adequate	1
		Documentation inadequate	0
M.	Dissolved oxygen:	Documentation adequate	1
		Documentation inadequate	0
N.	Stream flow:	Documentation adequate	1
		Documentation inadequate	0

Composite point score (A-N) = sum of points, normalized against the maximum possible and converted to a 0-9 scale.

* For example, pH, Eh analysis not appropriate for air samples.

CRITERION REPRESENTING CONTINUITY OF THE SAMPLING OR FIELD MONITORING PROGRAM

Component	Points
A. Total number of measurements for a particular parameter at a particular location (relative to the number considered adequate for characterization of the probability density function; considering the expected variability; all measurements in a set receive the same score):	
100% of required number of samples	3
≥ 50% of required number of samples	2
≥ 10% of required number of samples	1
< 10% of required number of samples	0

Objective criteria were used to assign "error rate" scores to a number of data sets in the present study. The "error rate" was defined as the proportion of samples in the data set which failed to meet the objective quality criteria. If the subjective scores for analytical methodology, quality assurance and sampling methodology are related to actual data quality, an inverse relationship to the "error rate" would be expected. Error rates were defined in terms of failure to meet the following objective criteria:

1. reported chemical concentrations greater than detection limit;
2. reported chemical concentrations greater than analytical error (if each concentration is reported with an associated analytical error);
3. mass balance - sum of reported concentrations less than the unit mass of the sample;
4. sum of dissolved concentrations less than the concentration of total dissolved solids;
5. anion-cation balance - sum of negative charge approximately equal to sum of positive charge;
6. dissolved concentration less than the total concentration for a given chemical constituent;
7. suspended concentration less than the total concentration for a given chemical constituent;
8. total organic carbon plus total inorganic carbon equals total carbon;
9. ratio of total organic carbon to total kjeldahl nitrogen greater than the lower limit in biota (5);
10. ratio of total organic carbon to total phosphorus greater than the lower limit in biota (35);
11. ratio of total dissolved solids (mg/L) to conductivity (umhos/cm^2) approximately 0.6 in dilute waters (conductivity less than 1,000 umhos/cm^2); and
12. reported concentrations consistent with expected ranges or ratios (statistically defined within a homogeneous data set).

Obviously, not all of the above criteria will be applicable to every data set. For example, anion-cation balance can only be expected in water samples with all major anion and cations analyzed. Similarly, conductivity and dissolved concentrations are only applicable to water samples. The criteria used for determination of "error rates" in each data set are discussed in greater detail as part of the data set evaluations which follow.

5.2.1 Nordic Main Seepage Water Data

The Nordic Tailings Management Area near Elliot Lake, Ontario is one of the best defined uranium tailings areas in Canada. Studies at this site began in the early 1970's and have continued to the present. Detailed hydrogeologic and geochemical studies of subsurface seepage from the Nordic Main tailings began in 1979. The 1979 study was carried out by Rob Blair, currently with Golder Associates, and data are compiled in Blair (1981) and Morin (1983). The 1980, 1981, 1982 and 1984 studies of Nordic seepage were performed by Kevin Morin, currently with Morwijk Enterprises; 1980-1982 data are compiled in Morin (1983). Nand Dave and Tjoe Lim of the Elliot Lake Laboratory of CANMET executed the 1983 study. The 1983 and 1984 data are compiled in Morin (in prep). Under contract to IEC BEAK, Morwijk Enterprises has made a detailed evaluation of data quality on the Nordic Main seepage water data, covering the 1979-1984 period.

The first phase of the data quality evaluation was to determine "laboratory (and field) evaluation scores" for analytical methodology, analytical quality control and sampling methodology. The subjective scoring system is described in Table 5.2.

Table 5.3 summarizes the scores for each year. The Process and Development Laboratory (PDL) of Rio Algom Limited performed analyses for all years except 1983. Scores for PDL on analytical methodology and analytical quality control were calculated from information supplied by PDL Chief Chemist, Mr. Jan Nipius. The 1983 scores for analytical methodology and analytical quality control were calculated from information supplied by Dr. Nand Dave of the Elliot Lake Laboratory of CANMET. Scores for sampling methodology were obtained from information in Blair (1981), Morin (1983) and Morin (in prep). The sampling methodology scores provide the basis for division of the data into four sets: 1979, 1980-1982, 1983 and 1984.

The second phase of the data quality evaluation involved graphical comparisons of pairs of parameters, such as pH and Fe. There are few comparisons for 1979 because few analyses were performed by PDL and fewer field pH's were taken. In many comparisons, general trends were defined and samples contradicting the general trend ("outliers") were apparent. Two major causes for outliers were analytical errors and geochemical effects. Six years of geochemical research at the site has provided a good understanding of these effects. Geochemical effects generally pertain to the existence of two bodies

TABLE 5.3: EVALUATION SCORES AND ERROR RATES FOR FOUR NORDIC DATA SETS

	1979	1980-82	1983	1984	1980-84 Average
Evaluation Scores (0-9)[1]					
Analytical Methodology	(6.2)	6.2	6.2	6.2	6.2
Analytical QC	(5.8)	5.8	6.4	5.8	6.0
Sampling Methodology	(4.0)	6.9	2.6	9.0	6.2
Error Rates (0-1)[2]					
Conductivity-pH Outliers	-	0.0063	0.0217	0	0.0093
Fe-pH Outliers	-	0	0.0652	0.0200	0.0284
Al-pH Outliers	-	0	0.0119	0	0.0040
Ra-226-pH Outliers	-	0.0182	0.0109	0.0200	0.0164
Fe-SO_4 Outliers	-	0.0155	0.0761	0	0.0305
Ion Balance-pH Outliers	-	0.0500	0.1196	0.1200	0.0965
Ion Balance-Conductivity	(0.3704)	0.0496	0.1196	0.1091	0.0928
Average Error Rate	-	0.0199	0.0607	0.0384	0.0396
Anion-Cation Balance	(0.3704)	0.1570	0.3370	0.1000	0.1980
Eh-pH Outliers	-	0	0.2391	-	0.1196
Na-pH Outliers	-	0	-	0	0
Ca-pH Outliers	-	0	-	0	0
NH_3-pH Outliers	-	0	-	0	0
Alkalinity-pH Outliers	-	0.0092	-	0	0.0046
Pb-pH Outliers	-	0	-	0	0
Ni-pH Outliers	-	0.0052	-	0	0.0026
Fe-Eh Outliers	-	0	0.2934	-	0.1467
Na-Fe Outliers	-	0	-	0	0
Na-Cl Outliers	-	0.0500	-	0	0.0278
Average Error Rate	(0.3704)	0.0204	0.1489	0.231	0.0506

1: 0 = poor, 9 = very good

2: 0 = no errors, 1 = errors in all samples

of groundwater at the site. Tailings-derived groundwater, which is the dominant groundwater in terms of quantity, displays well-defined geochemical trends with pH. A second, smaller body of groundwater is relatively dilute non-tailings-derived water (from surface infiltration or bedrock) or a mixture with tailings-derived water. This water often does not follow the general trend of tailings-derived water.

The third phase of the data quality evaluation involved the calculation of Error Rate Scores (ERS) for each data set. These scores, one for each comparison of two parameters, are considered to represent the "error rate" of the data set. The score is simply calculated from:

ERS = number of outliers attributed to error/total number of samples

Average error rate scores were computed for each of three data sets, 1980-1982, 1983 and 1984. Only parameter comparisons which were performed on all three data sets were used to compute the average.

Table 5.3 summarizes the error rate scores for each comparison, and the average scores for each data set. Figures A1 to A17 illustrating parameter relationships and identifying outliers are included in Appendix 5. Individual parameter comparisons, expected relationships between parameters and reasons for deviation from the general trend are discussed in the following paragraphs.

Field Conductivity vs. Field pH

In the 1984 comparison, outliers are exclusively the result of dilute water near the water table and bedrock; in other years, outliers are the result of both dilute water and measurement error.

Field Eh vs. Field pH

Outliers for the 1980-1981 comparison represent shallow (i.e., near the water table) piezometers. Outliers for 1983 are problematic. The Eh values are given as relative to the calomel reference. If true, the points below the outlier line are correct and points above the line are outliers. Yet the majority of points, which lie above the outlier line,

are correct if readings were referenced to the H_2 electrode. Apparently two different references may have been used in 1983. Values above the outlier line are assumed to be correct.

Dissolved Fe and (Fe^{2+}) vs. Field pH

The 1980-82 comparison shows a large scattering of points, but a general trend of increasing Fe with decreasing pH is apparent. Only one obvious outlier, the result of dilute water near the water table, exists for this data set. All the outliers for 1983 appear to be analytical errors. The 1984 comparison shows both dissolved Fe and the activity of free Fe^{2+} obtained from the WATEQ2 computer model (Ball et al., 1979) for speciation of dissolved Fe. The activity of Fe^{2+} displays the same general pattern as dissolved Fe, although vertical variation is reduced. Most of the 1984 outliers are from dilute waters.

Dissolved Na vs. Field pH

Morin (1983) identified Na and Cl as probable conservative tracers in Nordic Main seepage waters and used Na and Cl to define two sub-masses (acidic and pH-neutral) of tailings-derived water. As a result, a relationship between pH and Na was expected. Most of the outliers in the appendix figures are the result of the dilute water occurring near the water table and bedrock.

Dissolved Ca vs. Field pH

Most of the outliers are the result of dilute water.

Dissolved Al and (Al^{3+}) vs. Field pH

The sharp drop in dissolved Al as pH increases demonstrates the sensitivity of Al to pH. Values for (Al^{3+}) display a slightly sharper decrease as pH increases because of strong Al-OH complexing at neutral pH. No outliers were apparent.

Dissolved NH_3 vs. Field pH

NH_3 is a tailings-derived constituent and, thus, piezometers near the water table and bedrock should contain little NH_3. As expected, all outliers are from shallow and deep piezometers. The relatively high values of NH_3 in some outliers suggest some mixing with tailings-derived water.

Field Alkalinity vs. Field pH

Thermodynamics of the carbonate system stipulate that carbonate alkalinity increases sharply between pH 5.0 and 6.5. This increase is obvious on the plots in Appendix 5. Outliers are predominately from piezometers with dilute water and low alkalinity, and a few outliers are apparently measurement errors.

Dissolved Pb vs. Field pH

The solubility and mobility of heavy metals such as lead are known to increase with decreasing pH below neutral values. Concentrations of lead should, therefore, increase as pH drops from 7 to 4. This trend is evident on the 1980-82 plot in Appendix 5. However, the 1984 comparison apparently displays the opposite trend. The reason for this unusual behaviour is not known. None of the outliers are considered to be due to analytical error.

Dissolved Ni and (Ni^{2+}) vs. Field pH

Concentrations of Ni, like Pb, should be higher at acidic pH. The 1980-82 plot in Appendix 3 shows this trend, but the 1984 plot displays much scatter and a general trend is not readily apparent. The 1984 figure also shows the activity of free nickel. Like dissolved Fe and (Fe^{2+}), the variations in dissolved Ni are greater than those using (Ni^{2+}). Outliers are predominately from dilute water.

Dissolved Ra-226 vs. Field pH

Like heavy metals, Ra-226 concentrations (radioactivities) are often higher at acidic pH. This trend is apparent in all three sets of data. Outliers represent water near the water table, reflecting low-Ra infiltration, and a few analytical errors.

Dissolved Fe vs. Dissolved SO_4

In much of the Nordic Main seepage, Fe is the major cation and SO_4 is the major anion; only below 500 ppm does Fe cease to be the major cation. As a result, Fe and SO_4 should be close to a 1:1 molar ratio, otherwise there will be significant errors in the cation-anion balances (discussed below). All three data sets show the close relationship of Fe and SO_4. Outliers are the result of analytical errors in SO_4, which is analyzed gravimetrically (and through a Dionex in 1983) and is prone to error especially below 3,000 ppm. Figure A12.3 shows the effect of re-analysis of SO_4 for samples with originally incorrect concentrations. The effect of re-analysis is much more dramatic for the cation-anion balance (discussed below).

Dissolved Fe vs. Field Eh

The theoretical relationships of Fe to Eh are too varied and complex to discuss here. A simple conclusion based on these theoretical relationships is that a well-defined trend should not develop. Based on application of theory to Nordic Main seepage, a diffuse trend of decreasing Fe with decreasing Eh should be and is apparent. The unusual pattern on the 1983 plot is the result of the problematic 1983 Eh measurements (see Field Eh vs. Field pH).

Dissolved Na vs. Dissolved Fe

Because Na is a conservative tracer at the Nordic seepage site (see above, Dissolved Na vs. Field pH), Na is compared to Fe. A general trend is apparent, but significant scattering occurs, indicating a weaker relationship than seen on most comparisons. The weak trend causes difficulty in placing the outlier line. Outliers are all attributed to dilute water near the water table.

Dissolved Na vs. Dissolved Cl

Because both Na and Cl are conservative tracers at the Nordic Main site, graphical comparison of the two parameters should show a strong relationship. Outliers should only be the result of analytical errors. A strong relationship does appear on the two figures in Appendix 5. Outliers in 1980-82 are attributed to error. However, several marginal outliers in 1984 are samples at the water table, and are not attributed to error.

Error in Cation-Anion Balance

The error in the cation-anion balance is the first calculated parameter to be examined in detail in the Nordic data. The error is calculated here by the formula used in WATEQ2 (Ball et al., 1979):

$$ERR = ((CAT-AN)/0.5(CAT+AN)) \times 100\%$$

where CAT = sum of cations as epm (equivalents per million)
AN = sum of anions as epm

An ion balance error of ± 15% is usually considered acceptable. Using this criterion, an error rate score was calculated as the proportion of samples with "unacceptable" ion balance error.

However, the magnitude of ion-balance error expressed as a percentage of ionic strength is related both to conductivity and pH. A better way of comparing data sets with different pH or conductivity ranges would be in terms of outliers from the balance error-pH or balance error-conductivity relationships.

Error in Balance vs. Field pH

As explained above under Fe vs. SO_4, these two ions are the dominant anion and cation, respectively, in much of the Nordic Main seepage. Therefore, a significant error in the balance indicates an error in the Fe or SO_4 analysis at a particular pH. Most often, the error is in the SO_4 analysis.

The 1980-82 data set shows that 1982 data are much better than 1980 data, although both years have identical laboratory evaluation scores. All comparisons show that error in the balance increases with increasing pH (i.e., with decreasing conductivity, decreasing Fe, decreasing SO_4), because SO_4 analyses become more difficult and accuracy of other analyses (e.g., Ca, alkalinity) have a larger effect on the error.

Error in Balance vs. Field Conductivity

In agreement with Error vs. pH, error generally increases as conductivity decreases. The 1982 data again show less error than the 1980 data, although laboratory evaluation scores are identical. Five samples in 1984 with high errors were re-analyzed for SO_4 and the recalculated errors are much smaller. Therefore, SO_4 analysis accounts for much of the error. Sulphate analysis is more error-prone at lower concentrations. Outliers are predominately the result of SO_4 errors.

Comparison of Data Quality Scores

Objective error rate scores based on outlier frequency tend toward an inverse relationship with subjective quality scores for sampling methodology. The lowest sampling score (2.6) and highest average error rate score (0.0607) occur in the 1983 data set. The 1980-82 and 1984 data sets both have much better sampling scores and lower error rate scores, although their relative quality ranking depends on which score is used (Table 5.3).

Error rate scores based on unacceptable anion-cation balance also show an inverse relationship with sampling scores. The lowest sampling scores in 1983 and 1979 (2.6 and 4.0) correspond with the greatest error rates in ion balance (0.3370 and 0.3704), while the best sampling scores in 1980-82 and 1984 (6.9 and 9.0) correspond with the lowest error rates (0.1570 and 0.1000). However, error rate scores do not seem to exhibit any relationship to either the analytical methodology scores (which are constant at 6.2 in all years) or the scores for analytical quality control. This is true in spite of the fact that one suspected source of error is an analytical problem with SO_4.

5.2.2 Elliot Lake, Bancroft and Uranium City Data

The Elliot Lake and Bancroft areas in Ontario and the Uranium City area in Saskatchewan contain most of the uranium tailings sites in Canada. Extensive surveys of environmental conditions for revegetation of these sites were conducted from 1980-1981 by Ms. Margarete Kalin, then with the University of Toronto Institute for Environmental Studies, now with Boojum Research Ltd. The surveys were jointly funded by Environment Canada, Atomic Energy Control Board, and Energy, Mines and Resources, and have been

published in several Environment Canada reports (Kalin, 1981, EPS-5-WNR-81-1; Kalin, 1983, EPS-4-ES-83-1). The surveys resulted in a large set of chemical and radiochemical data for vegetation, tailings, tailings leachate and surface water on tailings. The largest portion of the data are for vegetation samples. Under contract to IEC BEAK, Boojum Research has conducted a detailed evaluation of data quality in this data set.

The first phase of the data quality evaluation was to determine "laboratory (and field) evaluation scores" for Analytical Methodology, Analytical Quality Control and Sampling Methodology. The subjective scoring system is described in Table 5.2. Scores were computed for three different subsets of the data, according to the three different analytical laboratories involved.

Table 5.4 summarizes the scores based on analytical and sampling documentation and protocol. Radiochemical analyses (radium-226 and lead-210) were performed at the University of Waterloo by Dr. H. Sharma. Lead, copper, nickel and cobalt were determined in all samples by Atomic Absorption Spectrophotometry (AAS) at the University of Toronto Institute of Environmental Studies. All other elements (cobalt, uranium, barium, strontium, dysprosium, iodine, bromine, magnesium, sodium, vanadium, aluminum, manganese, chlorine and calcium) were determined by Neutron Activation Analysis (NAA) at the University of Toronto, Chemical Engineering Department's Slowpoke Reactor Facility. Samples were collected, filtered and preserved in the field under the direction of M. Kalin.

The second phase of the data quality evaluation involved calculation of "error rates" for each subset of the data, according to the proportion of samples which failed to satisfy certain quality criteria. Each criterion and its application to the data are discussed in the following paragraphs. Table 5.4 summarizes "error rates" based on these criteria.

Concentrations Greater Than Detection Limit

Heavy metal parameters determined by Atomic Absorption Spectrophotometry were reported with a fixed detection limit for each matrix type (water, vegetation and tailings). Concentrations less than that limit were reported and entered into the data base, by convention, as zero. Computer programs utilizing the data would interpret zero for AAS parameters as a detection limit flag. Consequently, any value which lies

TABLE 5.4: EVALUATION SCORES AND ERROR RATES FOR THREE ELLIOT LAKE, BANCROFT AND URANIUM CITY DATA SETS

	Neutron Activation Analysis	Atomic Absorption Spectrophotometry	Radio-Chemical Analysis	Average
Evaluation Scores (0-9)[1]				
Analytical Methodology	7.7	3.1	7.7	6.2
Analytical QC	7.8	6.1	6.9	6.9
Sampling Methodology	7.0	7.0	7.0	7.0
Error Rates (0-1)[2]				
Distribution Outliers	0.0132	-	0.0101	0.0117
Regression Outliers	0.0076	-	0.0120	0.0098
Average Error Rate	0.0104	-	0.0111	0.0108
Concentration >Detection	-	0.0040	-	0.0040
Conc. >Analytical Error	0.0030	-	-	0.0030
Σ Concentrations < Mass	0.0070	-	-	0.0070
Dissolved Ra < Total Ra	-	-	0.2500	0.2500
Σ Concentrations < TDS	0.0610	-	-	0.0610
TDS < Total Solids	-	-	-	0.1560
TDS/Conductivity 0.5-0.7	-	-	-	0.3333
Average Error Rate[3]	0.0078	0.0040	0.0120	0.0084

1: 0 = poor, 9 = very good

2: 0 = no errors, 1 = errors in all samples

3: Dissolved radium and TDS were not included in the database and are therefore excluded from average error rate calculations.

between zero and detection limit constitutes a data reporting or entry error subject to misinterpretation. Table A1 in Appendix 5 shows the frequency of such errors for lead, nickel, copper and cobalt determinations.

Concentrations Greater Than Analytical Error

Radium-226 and lead-210 analytical results were reported as a concentration plus an analytical error unique to each sample. Analytical error is computed as a function of the counting statistics (Kalin, 1983). Both concentration and error were entered into the data base. Computer programs utilizing the data can easily compare each concentration to its associated error, interpreting any value less than its associated error as suspect. Consequently, there does not seem to be any basis for including such values in computation of an "error rate" for the data set. For radium-226 and lead-210 respectively, 4% and 6% of determinations were less than analytical error.

Elements determined by Neutron Activation Analysis were reported either as a detection limit (computed from background counts) or as a concentration with an associated analytical error (computed from peak and background counts). Under this system, concentrations less than analytical error should not be reported as concentrations. An integer code enables the computer to distinguish values which represent detection limits from those to be interpreted as actual concentrations. A computer scan of the data base was conducted to detect values coded as concentrations, but less than the associated analytical error. Four such values were found out of 1,143 samples scanned for 14 NAA element determinations. All four samples included magnesium determinations which had been corrected for aluminum interference to values less than analytical error, but not recoded as detection limits.

Mass Balance

Determinations on the Elliot Lake, Bancroft and Uranium City samples did not include all major elements. Silica and sulphur, for example, were not determined. Therefore, the sum of recorded concentrations on a gram per gram basis should not exceed the unit mass of the sample (1 gram). As a test of this expectation, all concentrations on each sample were converted to grams per gram and summed. The radionuclides were not included since their contributions were insignificant (on the order of 10^{-9} grams/gram). Loss on

ignition was included for tailings and soil samples. NAA values coded as detection limits were included in the summation. Missing values were included as zero concentrations. Out of 1,143 samples of all matrix types, eight samples were found which exceeded the mass balance criterion (sums greater than 1 gram).

Of the samples exceeding this criterion, five had high loss on ignition values (91 to 93%), and some also had high barium, aluminum, magnesium or calcium concentrations. A single sample is very probably the result of a data entry error. All eight samples were treated as errors for calculation of an "error rate" although seven sums are probably within a reasonable range of unity.

Sum of Dissolved Concentrations Less Than Total Dissolved Solids

Total dissolved solids (TDS) was determined for some water samples, but was not included in the computerized data base. However, it was possible to match TDS values (Kalin, 1983) with data base samples and to ascertain whether the sum of recorded chemical concentrations was less than the TDS determined by ASTM (1979) Standard Method D-1888-78. Out of 33 samples, the concentration sums exceeded TDS in two cases. The analytical error associated with TDS was not determined, but the discrepancies in both cases were greater than the 15 to 20% error range typically associated with TDS measurements. Both samples exceeding this criterion were considered to contain analytical errors, probably in TDS.

Reported Concentrations Consistent With Expected Ranges

Expected ranges for chemical parameters in soils and tailings are difficult to assess from the outside literature due to wide variability between areas. For the purposes of the present data evaluation, expected ranges were defined in terms of observed variability within each tailings area - Elliot Lake, Bancroft and Uranium City. Standard deviations for radium-226, barium and calcium in tailings from each area, and in soils from a control area, were calculated, and samples outside the range defined by the mean $\pm$ 3 standard deviations were considered outliers. In a normal population, 99.7% of all observations are expected to fall within this range. However, the frequency distributions in Figures A18 to A20 are generally skewed. This complicating factor has been ignored in computing "error rates" as outlier frequencies. Outlier frequencies are listed by chemical parameter and area in Table A2, Appendix 5.

Reported Concentrations Consistent with Expected Ratios

Relationships between parameters were defined within each area and sample type using linear regression techniques. Several highly significant relationships ($p < 0.001$) without non-linear trends were identified (Figures A21 and A22). Calcium and magnesium concentrations (both determined by NAA) were strongly related, as were radium-226 and lead-210 concentrations (both determined by radiochemical analysis). In each case, the standard deviation of residuals from the regression line was calculated, and the distribution of residuals examined. Outliers from the expected relationship were defined as samples with residuals beyond three standard deviations from the regression line. Outlier frequencies are listed by parameter relationship and area in Table A3.

Dissolved Radium-226 Less Than Total Radium-226

Dissolved radium-226 (from filtered water samples) and total radium-226 (from unfiltered samples) were determined at eight sampling points. Dissolved concentrations less than total concentrations or within analytical error of total concentrations were expected. Three times the mean analytical error of 1.33 pCi/L of radium-226 was used as the criterion for an acceptable excess of dissolved over total radium-226. Out of eight samples, two failed to meet this criterion, resulting in an "error rate" of 0.25. This estimate is based on a very small number of observations and may not be meaningful as a quantitative error rate.

Dissolved Solids Less Than Total Solids

Total dissolved solids (TDS) and total solids (TS) were determined in some water samples, but were not included in the computerized data base. However, the measurements were compared in 45 samples with both TDS and TS values. A TDS value less than the TS value or within analytical error of TS is expected. Since analytical errors associated with these measurements were not determined, a 15% analytical error was assumed. TDS exceeded TS by more than this amount in 7 out of 45 samples, for an "error rate" of 0.16.

Total Dissolved Solids vs. Conductivity

The ratio of total dissolved solids (TDS in mg/L) to conductivity (umhos/cm^2) approximates 0.6±0.1 in most dilute water samples, with conductivities less than about 1,000 umhos/cm^2 and low organic content. Water samples were selected from the data set, according to these criteria, for examination of TDS/conductivity ratios. Twelve samples with both TDS and conductivity measurements met the selection criteria. The mean TDS/conductivity ratio for these twelve samples was 0.6. In four samples, the ratio fell beyond the expected range of 0.5 to 0.7, resulting in an "error rate" of 0.33. Since this estimate is based on a very small number of eligible observations, it may not be meaningful as a quantitative error rate.

Comparison of Data Quality Scores

Few of the objective error rate scores were computed for more than one subset of the data. As a result, only the scores based on outlier frequency permit comparison with the subjective quality scores computed for the laboratories associated with each subset. The average outlier frequency score for radiochemical parameters (0.0111) exceeded the average for neutron activation analysis (0.0104). Subjective quality scores for the radiochemical and NAA laboratories differed only with respect to analytical quality control, with a higher score for NAA (7.8 vs. 6.9). The scores are, therefore, consistent with an inverse relationship between "error rates" and subjective data quality evaluations.

5.2.3 Grand River Basin Surface Water Data

The Grand River Conservation Authority (GRCA) conducted a water quality study of reservoirs in the Grand River Basin during the 1978-1979 period. Mr. Peter Mason (GRCA) was responsible for the sampling effort. Samples were then submitted to the Rivers and Lakes Laboratory of the Ontario Ministry of the Environment for analysis of physical, chemical and biological parameters, including total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC), total phosphorus (TP), suspended phosphorus (SP), total solids (TS), suspended solids (SS), conductivity, total kjeldahl nitrogen (TKN), chloride, sulphide, sulphate, iron, manganese, free ammonia and chlorophyll.

Data pertaining to three different reservoirs, Conestoga, Belwood and Guelph were obtained from GRCA for data quality evaluation by IEC BEAK. Samples from upstream and downstream of each reservoir were included with the reservoir data.

The sampling methodology evaluation was completed by GRCA according to the criteria described in Table 5.2. Sampling documentation is included in an unpublished GRCA report and in GRCA files.

The analytical methodology and quality control evaluations were completed by IEC BEAK in consultation with MOE personnel. Analytical methods were probably similar to those described in the recently published MOE Handbook of Analytical Methods (MOE, 1984). Analytical quality control activities have recently been described in the 1982-1984 Performance Report from Water Quality Section (MOE, 1985). Ms. Joan Crowther (River and Lakes Laboratory) has confirmed that the activities described in this report also applied during the 1978-79 period of the GRCA survey. Table 5.5 summarizes the subjective laboratory evaluation scores according to the criteria of Table 5.2.

The objective data quality evaluation involved calculation of "error rates" according to the proportion of samples which failed to satisfy certain quality criteria. The criteria and their application to the data are discussed in the following paragraphs. Table 5.5 summarizes the "error rates" based on these criteria.

Organic Carbon:Nitrogen Ratios

The ratio of total orgnic carbon (TOC) to total kjeldahl nitrogen (TKN) in water was expected to exceed the biological ratio, given by Wetzel (1975) as 5.7 for plants. To allow for analytical error, an expected ratio of five or greater was used as a criterion for acceptable data. Samples with lower ratios were considered to be in error. Such samples were found only in the Conestoga data.

Organic Carbon:Phosphorus Ratio

The ratio of TOC to total phosphorus (TP) in water was expected to exceed the biological ratio, given by Wetzel (1975) as 40 for plants. To allow for analytical error, an expected

TABLE 5.5: EVALUATION SCORES AND ERROR RATES FOR THE GRAND RIVER BASIN DATA

	Conestoga	Belwood	Guelph	Average
Evaluation Scores (0-9)[1]				
Analytical Methodology	5.2	5.2	5.2	5.2
Analytical QC	7.2	7.2	7.2	7.2
Sampling Methodology	7.2	7.2	7.2	7.2
Error Rates (0-1)[2]				
TOC:TKN >5	0.0673	0	0	0.0224
TOC:Total Phosphorus >35	0.0385	0	0	0.0128
TOC+TIC = TC	0.0426	0.0833	0.0926	0.0728
SP <Total Phosphorus	0.0159	0	0.0455	0.0205
SS< Total Solids	0.0189	0	0	0.0063
TDS/Conductivity 0.5-0.7	0	0.0357	0.0357	0.0238
ΣConcentrations TDS	0	0	0	0
Average Error Rate	0.0262	0.0170	0.0248	0.0227

1: 0 = poor, 9 = very good

2: 0 = no errors, 1 = errors in all samples

ratio of 35 or greater was used as a criterion for acceptable data. Samples with lower ratios were considered to be in error. Such samples were found only in the Conestoga data.

Carbon Balance

The sum of TOC and total inorganic carbon (TIC) was expected to equal the total carbon value. In most samples, this was true, with no error, indicating that one of the three parameters, probably TIC, was calculated from the others. However, in all three data subsets, a low proportion of errors was found, some of substantial magnitude. These were quite likely typographical or transcription errors.

Suspended Phosphorus Less Than Total Phosphorus

Suspended phosphorus (SP) should be less than total phosphorus (TP). Samples in which this was not the case were considered to be in error. Such errors were observed in low frequency in the Conestoga and Guelph data.

Suspended Solids Less Than Total Solids

Suspended solids (SS) should be less than total solids (TS). Where this was not the case, an error was considered to have occurred. The situation arose in a single Conestoga sample.

Total Dissolved Solids vs. Conductivity

Total dissolved solids (TDS) was calculated for each sample by subtraction of suspended from total solids. The ratio of TDS (in mg/L) to conductivity (umhos/cm^2) approximates 0.6 ± 0.1 in most dilute water samples, with conductivities less than about 1,000 umhos/cm^2 and low organic content. All samples met this definition of dilute water. Several samples with TDS/conductivity ratios outside the 0.5 to 0.7 range were observed in the Belwood and Guelph data.

Sum of Dissolved Concentrations Less Than Total Dissolved Solids

All major elements were not determined in these samples. Consequently, the sum of measured concentrations should not exceed the total dissolved solids (TDS) except when gross measurement errors, typographical or transcription errors have occurred. No such errors were observed in any sample.

Comparison of Data Quality Scores

Average "error rates" for each data subset (Table 5.5) differ very little from one subset to another, ranging from 0.017 for Belwood to 0.026 for Conestoga. This variation cannot be related to variation in the subjective quality scores based on laboratory and sampling evaluations (Table 5.2), since all three data subsets were generated under identical sampling and analytical conditions.

5.2.4 Niagara Basin Surficial Sediment Data

A survey of the geochemistry of surficial sediments in the Niagara Basin of Lake Ontario, west of the Niagara River mouth, was undertaken by the Canada Centre for Inland Waters (CCIW) in 1969. A total of 281 sediment samples were taken from a study area covering approximately 150 km^2. A summary of some of these data has been published (Sly, 1983), and the raw data are available from CCIW in unpublished form (Sandilands and Sly, 1977). The data include all major elements analyzed by x-ray fluorescence (Fe_2O_3, CaO, P_2O_5, MgO, SiO_2, TiO_2, K_2O, Na_2O, S, MnO, Al_2O_3), trace elements analyzed by atomic absorption spectrophotometry, particle size parameters, organic and inorganic carbon, temperature, pH and Eh. The data were obtained from CCIW for data quality evaluation by IEC BEAK.

Evaluation of sampling, analytical methodology and quality control was conducted by IEC BEAK in consultation with CCIW personnel. Sampling and analytical methodology are described in Sandilands and Sly (1977). Table 5.6 summarizes the subjective laboratory evaluation scores according to the criteria of Table 5.2.

The objective data quality evaluation involved calculation of "error rates" according to the proportion of samples which failed to satisfy certain quality criteria discussed in the following paragraphs. Error rates based on these criteria are included in Table 5.6.

Sum of Gravel, Sand, Silt and Clay Fractions

The gravel, sand, silt and clay fractions, defined as grain size categories, should include the entire sample and should, therefore, sum as percentages to 100%, allowing for rounding error. Percentages were reported to two significant decimal places and 0.01% was allowed for rounding error. All 281 samples conformed to this criterion.

Sum of Major Elements

The sum of major element concentrations (in percent), plus organic and inorganic carbon concentrations (TOC and TIC), should not exceed 100% of the sample mass. All 281 samples conformed to this expectation.

Reported Concentrations Consistent with Parameter Relationships

Relationships between certain measured parameters in sediments are expected. Samples which do not conform to these relationships can be identified as outliers. Outliers do not necessarily represent sampling, analytical or data reporting errors; however, they are suspect as errors unless they can be explained in terms of known heterogeneity in the study area. All outliers from statistically significant ($p < 0.001$) linear relationships were treated as errors in calculation of an "error rate" for the Niagara Basin data set.

Least squares regression techniques were used to define inter-parameter relationships. A residual deviation from the linear regression line was computed for each sample. The standard deviation of residuals was calculated and samples falling more than three standard deviations from the regression line were considered outliers. Analysis of variance was used to test the significance of the linear regression, and a Durbin-Watson test was performed as a check for non-linear trends.

Five inter-parameter relationships were investigated. In each case, linear relationships were expected. Dependence of mercury concentration (Hg) on clay content results from sorption processes and has been reported by Thomas (1972, 1974), Fitchko and Hutchinson (1975) and Thomas and Jaquet (1976) in other sediment studies. Clay content should be related to mean particle size (Psize) since the clay fraction is defined in terms of particle size. Total organic carbon (TOC) should be related to phosphorus (P_2O_5) since

TABLE 5.6: EVALUATION SCORES AND ERROR RATES FOR THE NIAGARA BASIN DATA

Evaluation Scores (0-9)[1]	
Analytical Methodology	7.3
Analytical QC	6.3
Sampling Methodology	6.5
Error Rates (0-1)[2]	
Sum of Grain Size Fractions = 1	0
Sum of Major Element Fractions < 1	0
Hg - Clay Outliers	0.0070
Clay - Particle Size Outliers	0.0140
Organic Carbon - P_2O_5 Outliers	0.0110
Zn - Organic Carbon Outliers	0.0070
Hg - Organic Carbon Outliers	0.0180
Average Error Rate	0.0080

1: 0 = poor, 9 = very good

2: 0 = no errors, 1 = errors in all samples

phosphorus is a limiting nutrient for biota. Dependence of zinc concentration (Zn) on TOC results from sorption processes and has been reported by Peyton et al. (1975), Mothersill and Fung (1972) and Kemp et al. (1976). Sorption processes also account for the dependence of Hg on TOC, as reported by Kennedy (1971), Thomas (1972), Thomas and Jaquet (1976) and Kemp et al. (1976).

Outliers from each of these relationships were identified. Residual distributions and outliers from the Hg-clay, clay-Psize, TOC-P_2O_5, Zn-TOC and Hg-TOC relationships are shown in Figures A23-A27, Appendix 5. Error rates are summarized in Table 5.6.

5.3 Application of Criteria for Data Base Evaluation

Within major data sets, error rates can be estimated on a common basis for various subsets of the data, and related to subjective evaluation scores. In the Nordic data, for example, eight error 'tests' can be performed on each of three data subsets representing different time periods. Error rates averaged over these eight tests correlate with the sampling evaluation scores which exhibit the greatest degree of variation between time periods.

Among unrelated data sets, however, comparisons are complicated by the existence of quite different suites of parameters in each set. The type of error test is constrained by the available parameters, so that different tests contribute to each average error rate. Consequently, average 'error rates' may not be comparable among data sets.

Figure 5.1 illustrates the relationship between average error rates and subjective evaluation scores. There is considerable scatter around the line which follows the mean of the three evaluation scores for each data set. This line suggests a weak inverse relationship between error rate and evaluation score.

The range of evaluation scores was quite narrow for the data sets used in this study. A wide range of scores would have permitted more definitive conclusions. The observed relationship provides some justification for using subjective evaluation scores as a rough indication of probable data quality, however, additional verification of the evaluation system by application to other data sets is advised.

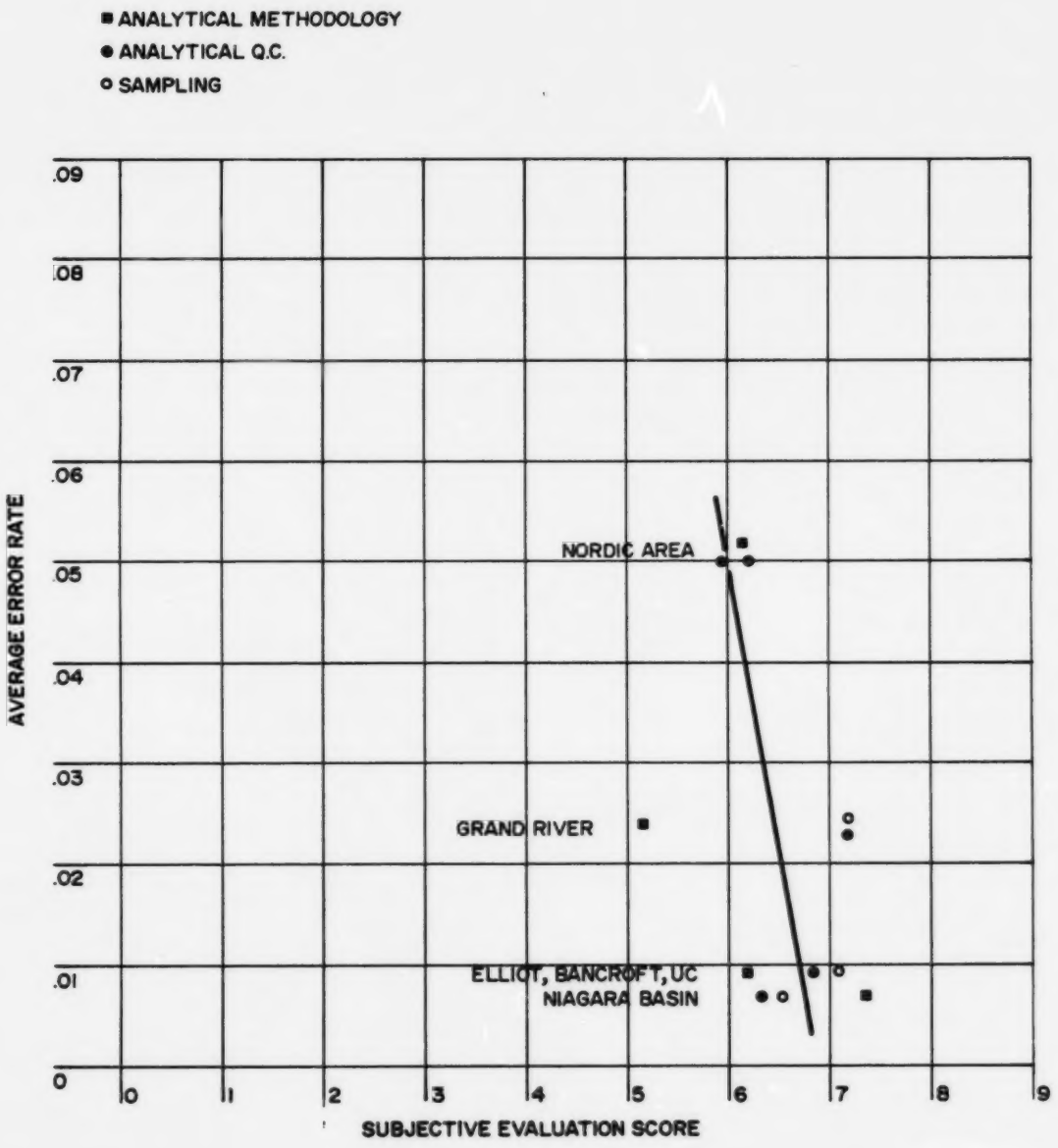
Subjective evaluation scores should be applied with an understanding that they can only reflect probable data quality on the basis of general lab or sampling practice. Specific technique can be an important quality determinant which is not amenable to assessment. Appropriate and well documented methods, if not performed exactly, can produce low quality data. This may account for the high error rates associated with TDS or dissolved vs. total radium-226 in the Elliot Lake, Bancroft, Uranium City data, which otherwise seems to be of high quality. This example also emphasizes the importance of logical data checks, since the suspect measurements had been identified and eliminated from the data base prior to this study.

Inclusion of performance measures in the subjective evaluation system will reflect consistent poor performance, however, there is no guarantee that poor performance will be consistent. In fact, interlaboratory performance measures may not reflect routine lab performance. Field performance measures are entirely lacking from the subjective evaluation system. Field technqiue is more difficult to assess on an interlaboratory basis.

Since the subjective evaluation scores are inferential, and at best approximate, they should be applied only as a first step in selection of data from a larger data set. A set of data selected on the basis of high evaluation scores is expected to be of high quality but may still be subjected to more objective quality tests. A low evaluation score whould not automatically eliminate a particular block of data from consideration if the amount of otherwise suitable data is limited. Similarly, no data should be irretrievably discarded from a data set, solely on the basis of subjective evaluation scores.

FIGURE 5.1

Relationship of Average Error Rates and Evaluation Scores



6.0 RECOMMENDATIONS

1. Subjective evaluation scores based on general laboratory and sampling protocol can be expected to reflect probable data quality to some extent.

2. Such scores should be used only as a first step in selecting data from a set which is larger than required, and should not preclude the use of more objective data quality checks on the selected data.

3. Data subsets should not necessarily be eliminated from consideration solely on the basis of subjective evaluation scores, and should not be eliminated from a data base on this basis alone.

4. A multiple (4) criterion system is recommended, such as the system described in general in Table 4.1 and quantified in Table 5.2, including evaluations of:

   a) analytical methodology,
   b) analytical quality control,
   c) sampling and handling, and
   d) continuity of data.

   The last criterion reflects data quantity rather than quality and must be defined in relation to specific project requirements.

5. All criteria should be quantified on a simple numeric or alphabetic scale.

6. The quantification system in Table 5.2 should be subjected to additional verification by application to other data sets and correlation of objective and subjective quality scores. Any new quantification system should undergo similar verification prior to incorporation in a data base.

7. Documentation in support of evaluation scores assigned to particular blocks of data should be maintained on file, and updated, with score revision if necessary, every 5-10 years.

7.0 REFERENCES

Anon. 1947. Chemical procedures for the estimation of uranium in ores, etc. used at the Bureau of Mines, Ottawa Laboratories. Bureau of Mines, Ottawa, October 22.

APHA. 1980. Standard Methods for the Analysis of Water and Wastewater, 15th edition. American Public Health Association, Inc., New York.

Ashbrook, A.W. 1971. The spectrophotometric determination of uranium in ores, residues and other materials. Mines Branch, Ottawa, Information Circular IC266.

Ball, J.W., E.A. Jenne, and D.K. Nordstrom. 1979. WATEQ2 - A computerized chemical model for trace and major-element speciation and mineral equilibria of natural waters. IN: Chemical Modelling in Aqueous Systems, edited by E.A. Jenne, American Chemical Society Symposium Series 93. p. 815-835.

Barkley, D.J. and J.A.F. Bouvier. 1974. Thorium - spectrophotometric, ion exchange separation (method). In: A Manual of Analytical Methods used by the Canadian Mining Industry - Part II. Published by the Canadian Mineral Analysts.

Blair, R. 1981. Hydrogeochemistry of An Inactive Pyritic Uranium Tailings Basin, Elliot Lake, Ontario. M.Sc. Thesis, Department of Earth Sciences, University of Waterloo. 125 p.

Bouvier, J.A.F. and R.J. Guest. 1958. The "thorin" colorimetric method for thorium determinations: effect of some common ions, and methods for overcoming interferences. Mines Branch, Ottawa, Research Report R34.

Brooks, F.H. 1959. Thorium - colorimetric. In: Handbook of Analytical Methods. Consolidated Denison Mines Ltd., Elliot Lake, Ontario.

Bruce, J.P. and R.H. Clark. 1966. Introduction to Hydrometeorology. Pergamon, London.

Burstall, F.H. and A.F. Williams. 1950. Handbook of chemical methods for the determination of uranium in minerals and ores. London, Her Majesty's Stationery Office.Canadian Mineral Analysts. 1972. A manual of analytical methods used by the Canadian mining industry - Part I.

Canadian Mineral Analysts. 1972. A manual of analytical methods used by the Canadian mining industry - Part II.

Chase, W.L. 1948. Unpublished method sheet.

Cherry, J.A., R.W. Gillham, E.J. Reardon, J.F. Barker, P. Fritz, J.P. Greenhouse and S.K. Frape, 1984. Short Course: Field Methods in Contaminant Hydrogeology. University of Waterloo, Groundwater Research Institute, Waterloo (unpublished).

Chow, V.T. 1968. Open Channel Hydraulics. McGraw-Hill.

Chung, K.S. and J.P. Riley. 1963. A scheme for the analysis of monazite and monazite concentrates. Anal. Chem. Acta. 28: 1-29.

Convey, J. (ed.). 1957. The milling of Canadian ores. 6th Commonwealth Mining and Metallurgical Congress.

Dreesen, D.R., E.S. Gladney and J.W. Owens, 1979. Interlaboratory comparison of arsenic molybdenum and selenium analyses from uranium mill tailings. Journal of the Water Pollution Control Federation. 51:2447-2456.

Environment Canada. 1982. Historical streamflow summary, Ontario. Ottawa.

Environment Canada. 1983. Sampling for water quality. Water Quality Branch, Inland Waters Directorate, Ottawa.

EPA. 1977. Proceedings Manual for Groundwater Monitoring at Solid Waste Disposal Facilities. EPA/530/SW-611.

Faye, G.H., W.S. Bowman and R. Suturno. 1979. Uranium ore BL-5 - a certified reference material. Canada Centre for Minerals and Energy Technology, Report No. MRP/MSL 79-22 (R).

Fisher, J.W. 1974. Thorium - spectrophotometric (method). TTA extraction and fluoride separation. In: A Manual of Analytical Methods used by the Canadian Mining Industry. Loc. cit.

Fitchko, J. and T.C. Hutchinson. 1975. A comparative study of heavy metal concentrations in river mouth sediments around the Great Lakes. J. Great Lakes Res. 1:46-78.

Florence, T.M., P. Pakalus and L.S. Dale. 1972. Comparative survey of methods for the determination of uranium in ores. Australian Atomic Energy Commission, Lucas Heights, Australia, Report No. AAEC/E237.

Gillham, R.W., M.J.L. Robin, J.F. Barker and J.A. Cherry. 1983. Groundwater monitoring and sample bias. API Publ. 4367.

Golder Associates. 1977a. Geotechnical investigation - Strike Lake tailings impoundment, Elliot Lake, Ontario - Volume II. (22 borehole samples). November 1977.

Golder Associates. 1977b. Sub-surface investigation, proposed Evans Lake protection, Quirke Mines tailings disposal area, Elliot Lake, Ontario - August 1977 (6 borehole samples).

Golder Associates. 1978. Geotechnical investigation, existing Quirke Mine tailings management area - Volume I, Elliot Lake, Ontario - March 1978 (37 borehole samples).

Golder Associates. 1979. Supplementary data, Strike Lake tailings impoundment, Elliot Lake, Ontario - April 1979 (13 boreholes, 8 test pits and 10 probes).

Gulf Minerals. 1981. Annual Environmental Report - 1981. (90 air, water, soil and plant samples).

Gulf Minerals. 1982. Annual Environmental Report - 1982. (309 air and water quality samples).

Hilliard, T.R. (ed.). 1965. Radiological water pollution in the Elliot Lake and Bancroft areas. Province of Ontario, Deputy Ministers Committee.

Hume, D.N. 1973. Pitfalls in the determination of environmental trace metals. Progress in Analytical Chemistry 5: 3-16.

Hunt, E.C., G.W.J. Kingsbury and A.T. Williams. 1950a. Microassay of thorium and uranium in ores by chromatographic separation with spectrographic determination of the thorium, (British). Atomic Energy Research Establishment, Harwell, Report No. CRL/AE75.

Hunt, E.C., G.H. Smith and A.F. Williams. 1950b. New chromatographic procedures for the determination of thorium and uranium in minerals and ores. ibid. Report No. CRL/AE70.

IUPAC. 1971. Commission on radioanalytical chemistry and nuclear materials. Preparation of reference samples for uranium in low grade ores. Pure and Applied Chemistry, 27: 291-304.

Ingles, J.C. 1951. The determination of thorium in its ores. Mines Branch, Ottawa, Memorandum Series 110, Can. Chem. Proc. Ind. 35: 397.

Ingles, J.C. 1959. Manual of analytical methods for the uranium concentrating plant. Ottawa, Queen's Printer, Monograph 866.

Ingles, J.C. 1959. loc. cit. (uranium).

Ingles, J.C., R. Suturno, W.S. Bowman and G.H. Faye. 1977. Radioactive ores DH-1, DL-1, BL-1, BL-2, BL-3 and BL-4 - certified reference materials. CANMET, Ottawa.

Ingles, J.C. et al. 1977. loc. cit. (uranium).

Ingles, J.C. 1984. Chronological synopsis of analytical practices at the Bureau of Mines Laboratory. Prepared by J.C. Ingles, Consultant, for IEC Beak Consultants Ltd.

Josephson, J., 1984. Independent evaluation of monitoring data. Env. Sci. Technol. 18:11A-12A.

Kalin, M. 1981. A Preliminary Assessment of the Environmental Conditions of Two Abandoned Mill Tailings Sites in Saskatchewan. EPS 5-WNR-81-1, Environment Canada, Ottawa.

Kalin, M. 1983. Long-term Ecological Behaviour of Abandoned Uranium Mill Tailings 1. Synoptic Survey and Identification of Invading Biota. EPS 4-ES-83-1, Environment Canada, Ottawa.

Keith, L.H., W. Crummett, J. Deegan, Jr., R.A. Libby, J.K. Taylor and G. Wentler, 1983. Principles of environmental analysis. Anal. Chem. 55:2210-2218.

Kemp, A.L.W., R.L. Thomas, C.I. Dell and J.-M. Jaquet. 1976. Cultural impact on the geochemistry of sediments in Lake Erie. J. Fisheries Research Board. 33:440-462.

Kennedy, E.J., R.R. Ruch and N.F. Shimp. 1971. Distribution of mercury in unconsolidated sediments from southern Lake Michigan. Environmental Geology Notes, No. 44, Illinois State Geological Survey, Urbana.

Laxan, D.P.H. 1977. A specific conductance method for quality control in water analysis. Water Research, 11, p. 91-94.

Lendrum, F.C. 1970. Developments in Canadian uranium milling practice. Journal of Metals, American Institute of Mining and Engineering, July 1970.

Miedema, M.C., 1983. The reporting of results from the analytical laboratory. Report of the Analytical Subcommittee of the Canadian Uranium Producers Metallurgical Committee, ASCUPMC-1.

MacLaren. 1978. Environmental assessment of the proposed Elliot Lake uranium mines expansion - volume 2. Background information update - February 1978. (201 air, water and fish samples).

Mayling, A.A. 1958. Assay office annual report. Consolidated Denison Mines Ltd., Elliot Lake.

MOE (a). Cardiff area radiological program (21 water qualilty samples).

MOE (b). Radiological monitoring - Bancroft area - Appendix B (22 water quality samples).

MOE (c). Radiological monitoring - Bancroft area - Appendix A (59 water quality samples).

MOE (d). Radiological results - Cardiff area - 1977 (221 water quality samples).

MOE (e). Radioactive sampling - Cardiff area (83 water quality samples).

MOE (f). Cardiff radioactive study (76 water quality samples).

MOE (g). Radiological survey - Bancroft area (77 water quality samples).

MOE (h). Water sampling for the Ministry of the Environment radiological survey (21 water quality samples).

MOE (i). Water samples for the environment radiological survey (73 water quality samples).

MOE (j). Cardiff radiological program - September 14, 1982 (44 water quality samples).

MOE (k). Cardiff radiological program - October 19, 1983 (46 water quality samples).

MOE. 1985. 1982-1984 Performance Report from Water Quality Section. Laboratory Services Branch, Ministry of the Environment.

Morin, K.A. 1983. Prediction of Subsurface Contaminant Transport in Acidic Seepage From Uranium Tailings Impoundments. Volumes I and II. Ph.D. Thesis, Department of Earth Sciences, University of Waterloo. 713 p.

Morin, K.A. In preparation. 1984 Geochemical Study of the Acidic contaminant Plume near the Nordic Main Uranium-Tailings Impoundment, Elliot Lake, Ontario: Final Report. Energy, Mines and Resources Contract No. 26SQ.23241-4-1689.

Mothersill, J.S. and P.C. Fung. 1972. The stratigraphy mineralogy, and trace element concentrations of the quarternary sediments of the northern Lake Superior basin. Can. J. Earth Sciences. 9:1735-1755.

National Lead Co. of Ohio. 1958. Summary of analytical procedures for the determination of impurities in uranium concentrates. Cincinnati, Ohio.

OWRC. 1966. Interim report on "Radiological Water Pollution in Elliot Lake and Bancroft Areas". Ontario Water Resources Commission.

OWRC. 1971. Water pollution from the uranium mining industry in the Elliot Lake and Bancroft areas, Volume 1 - Summary. Ontario Water Resources Commission - Volume 1, October 1971.

OWRC. 1972. Water pollution from the uranium mining industry in the Elliot Lake and Bancroft areas, Volume 2 - Detailed Findings. Ontario Water Resources Commission, March 1972.

Ozga, W.J. 1979. Supplying data to users. Environment Canada Tech. Bull. III, Ottawa.

Peyton, T. and A. McIntosh. 1975. A field study on the distribution of aerially deposited trace elements in an aquatic ecosystem. I. Sediment component, in Trace Substances in Environmental Health, Vol. III, D.D. Hemphill, ed., University of Missouri Press.

Pickett, D.E. 1978. Milling practice in Canada. Canadian Institute of Mining and Metallurgy, Special Volume 16.

Rabbits, F.T. 1947. Unpublished method sheet. Mines Branch, Ottawa.

Rabbits, F.T. 1949a. Determination of uranium in ores, modified mercury cattiode - cupferron method. Mines Branch, Ottawa, Memorandum Series 103.

Rabbits, F.T. 1949b. The determination of U_3O_8 in ores and solutions, cellulose column method. Mines Branch, Ottawa, Memorandum Series 105.

Rabbits, F.T. 1952. Determination of uranium in ores. Bull. Can. Inst. Min. Met., 45: 27.

Radioactivity Division. 1950. Unpublished method sheet. Mines Branch, Ottawa.

Robson, F.P. 1950. Methods of analysis used in the Radioactivity Division of the Mines Branch. Mines Branch, Ottawa, Topical Report 48/50.

Rodden, C.J. and N.H. Furman. 1946. Manual of analytical methods, Vol. I. Madison Square Area, Corps of Engineers (declassified Report A2912).

Rodden, C.J. and N.H. Furman. 1946. loc. cit. (thorium).

Rodden, C.J. and J.J. Tregoning. 1950. Manual of analytical methods for the determintion of uranium and thorium in their ores. 1st Ed.

Rodden, C.J. and J.F. Tregonig. 1950. loc. cit., Method 7.

Saari, R. 1960. The influence of platinum ware on fluorimetric results. Dyno Mines Ltd., Bancroft, Ontario.

Sandilands, R.G. and P.G. Sly, 1977. Data listings of surficial sediment samples from grid sampling studies on the Great Lakes. Unpublished report, Canada Centre for Inland Waters.

Scheider, W.A., C.M. Cox and L.D. Scott. 1983. Hydrological data for lakes and watersheds in the Muskoka-Haliburton study area (1976-1980). Water Resources Branch, Ontario Ministry of the Environment. Report No. DR 83/6.

Shimp, N.F., J.A. Schleicher, R.R.Ruch, D.B. Heck and H.V. Leland. 1971. Trace element and organic carbon accumulation in the most recent sediments of southern Lake Michigan. Environmental Geology Notes No. 41, Illinois State Geological Survey, Urbana.

Sly, P.G., 1983. Sedimentology and geochemistry of recent sediments off the mouth of the Niagara River, Lake Ontario.

Smart, B.C. 1960. Seventh (Eldorado) analytical committee meeting (Port Hope). Eldorado Mining and Refining Ltd., Port Hope, Ontario.

Smith, C.W. and H.F. Steger. 1983. Radium-226 in certified uranium reference ores DL-1a, BL-4a, DH-1a and BL-5. CANMET Report 83-9E. Canada Centre for Mineral and Energy Technology.

Smith, C.W. 1983. Radioisotope activities in uranium tailings reference materials UTS-1 to UTS-4: Results of an interlaboratory program. CANMET Report MRP/MSL 83-112 (TR), Canada Centre for Mineral and Energy Technology, Minerals Research Program, Mineral Sciences Laboratories.

System House Ltd. 1983. National Uranium Tailings Program data standards manual. 14 p.

Thomas, R.L. 1974. The distribution and transport of mercury in the sediments of the Laurentian Great Lakes system. Proc. International Conference on Transport of Persistent Chemicals in Aquatic Ecosystems. National Research Council, Ottawa.

Thomas, R.L. 1972. The distribution of mercury in the surficial sediments of Lake Huron. Can. J. Earth Sciences. 10:194-204.

Thomas, R.L. and J.-M. Jaquet. 1976. Mercury in the surficial sedimetns of Lake Erie. J. Fisheries Research Board. 33:404-412.

Tsivoglu and O'Connell. 1962. Waste guide for the uranium milling industry. Robert A. Taft Sanitary Engineering Center, Cleveland, Ohio.

VanLoon, J.C. 1974. How accurate are environmental data? Chemistry 47(3): 18-19.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia.

Worlbec, A. 1950-80. Canadian Mines Handbook, Northern Miner Press, Annual Issues.

Zimmerman, J.B. and J.A.F. Bouvier. 1955. Measurement of thorium in ores by the thorium emanation method. Mines Branch, Ottawa, Technical Paper 14.

Zimmerman, J.B. and V.C. Armstrong. 1976. The determination of radium-226 in uranium ores and mill products by alpha energy spectrometry. CANMET, Ottawa, CANMET Report No. 76-11.

Zimmerman, J.B. and V. Reynolds. 1974. The determination of low concentrations of uranium in ores and solid mill products by x-ray fluorescence spectrometry. Mines Branch, Ottawa, Report TB197.

PROCEDURES FOR EVALUATION OF DATA IN ENVIRONMENTAL DATABASES, WITH PARTICULAR REFERENCE TO URANIUM TAILINGS

Serial No. 0SQ84-00033

Addendum: to replace pages 3.20 to 3.23 inclusive

3.2.3.2 Continuity of Sampling and Field Measurements

For long-term predictive modelling purposes, an understanding of both spatial and temporal variation in measured parameters is essential. This understanding is incorporated into the predictive process either in the form of probability density functions associated with each parameter in a stochastic model, or in defining boundaries for systematic variation of parameters during sensitivity analysis of deterministic models. An understanding of temporal variability can only be achieved by a continuous sampling program with repeated measurements at the location and over the time period of interest.

The continuity of the sampling effort, as represented in any database, can be assessed from the frequency of repeated measurements for a particular parameter at a particular location. Similar assessment techniques could be applied to chemical parameters or associated field measurements. For chemical parameters, concentrations measured in differently treated samples must be considered different parameters. Likewise, field measurements by different methods, such as automatic versus manual water level recordings, should be considered different measurements.

Consideration of sampling continuity as an aspect of data quality stretches the definition of "quality" to include the concept of "quantity". However, both concepts are relevant to the usefulness of the data for statistical modelling purposes. The logical distinction between these concepts should probably be retained by development of a separate evaluation criterion to represent the continuity of the sampling program. This criterion will be of particular use to the stochastic modeller in retrieving sets of repeated measurements, and should be defined in relation to the data requirements of particular modelling applications.

A sampling continuity factor could be calculated by normalizing the frequency of repeated measurements against some maximum value considered adequate for characterization of the probability density function within a particular region or time period. For example, if 50 measurements are considered adequate, 20 measurements of dissolved As concentration at the same location would each receive a continuity score of 0.4. Fifty or more measurements would all be assigned a perfect score of 1. Scores could change with addition of new data to the database or with the modelling requirements of the user, and would have to be recalculated periodically.

3.2.4 Streamflow Records

Any long-term modelling of the geochemical behaviour of radionuclides and trace elements from uranium mine tailings requires an understanding of the mass balance of the particular element under consideration. In order to obtain mass balance data, it is necessary to know both concentration and flow information. The following section presents a discussion of flow data as measured for environmental samples in Canada.

Description of Methods

Streamflow data are available from a variety of sources including Federal and Provincial government agencies as well as various private organizations. In spite of the diversity of sources, manual hydrometric methods have not changed appreciably in historical time (Environment Canada, 1982). Automatic continuous recording gauges of the float and drum type have been widely used since the mid-1900's. More recently, pressure transducer gauges have become available.

Manual and automatic methods are used for recording water level information, either singularly or as a combination. The manual method often relies on a vertical gauge staff calibrated in centimetres which is located at the station on the stream bank or attached to hydraulic structures. The total length of at least one staff must exceed the maximum expected flood level. An individual operator normally makes one or more observations of the flow stage (stage being the water surface elevation) per day to obtain a daily mean value (Bruce and Clark, 1966; Environment Canada, 1982). Wire weight, contact tape or pin gauges may be used in lieu of a staff gauge, or direct water level readings may be obtained with a surveyor's level.

The automatic method relies on a continuous water elevation or stage recorder. The stage is recorded on a roll chart for periods of up to one year in duration. The recorder is usually situated on the river bank so that it is protected from flooding and/or ice damage. Manual gauges may also be located at a recorder site so that data accuracy and equipment operation can be periodically assessed (Bruce and Clark, 1966).

At each hydrometeric station, it is necessary to measure water depth at about 20 points across the river section; flow velocity at each depth profile; air and water temperature; and/or ice thickness when appropriate (Ozga, 1979). For larger rivers, more than 20

depth measurement points are advisable; for small streams fewer points may be adequate.

The repeated measurement of the noted variables yield information on the stage and discharge for the construction of a stage-discharge rating curve. Thus, for each stage observation, one can interpolate a corresponding discharge from the rating graph. Periodic checking of discharge is necessary to confirm the validity of the observations and the record.

If changes in flow conditions are obvious, or if the measurements versus the rating curve deviate significantly, then the stage-discharge relationship has to be redefined (Bruce and Clark, 1966; Environment Canada, 1982). Stage discharge relationships should be determined during the open water season and backwater corrections applied during winter periods.

Sources of Error

Error can be associated with the hydrometric method that is used or with general and specific field conditions at or near the gauge or flow measurement sites.

There are two major disadvantages associated with any form of manual gauging. Firstly, the reliability of the record is entirely dependent on the accuracy of the operators' measurements. In some cases, erroneous observations can escape detection from the record. Secondly, measurements are normally taken one or more times per day. Periodic measurement in a quick-reponse stream poses a serious problem since discharge in a stream can change dramatically over a short space of time. It is possible, therefore, that a major flow event or other variations in discharge will not be recorded. The result will be a distorted record of daily and perhaps monthly average discharges (Bruce and Clark, 1966). The aforementioned problems are eliminated with the use of a continuous recording device, since all flow levels are recorded.

Regardless of the method employed, one of the most critical factors affecting the validity of a flow record is control. Control refers to the downstream conditions that will influence the stage-discharge relationship at a gauge station. Rapids, lakes, weirs and dams, ice conditions and changes in natural vegetation, in addition to channel morphology changes, are factors that affect control. Where control is deemed to be

stable at the gauging and stream flow measurement sites, then the stage-discharge relationship will be stable. However, changes due to erosion or deposition, or changes in base level and so on, necessarily result in control changes. Where the control is unstable and subject to change, frequent discharge measurements become necessary to allow for modification of the rating curve for a station. Accuracy in this case becomes a function of the frequency of repeated measurements (Bruce and Clark, 1966; Environment Canada, 1982), as well as measurement accuracy and nature of control changes.

At a station, ice conditions influence the stage-discharge relationship since the flow regime is altered when compared to an open water state. Ice cover, stream intersections, dams and lakes cause a backwater effect that must be compensated for, by assessing water surface slope, temperature records, and coincident water level and discharge measurements, to obtain a corrected stage-discharge relationship (Bruce and Clark, 1966).

The ideal point for measurement is where a channel constriction forms a hydraulic control point (Chow, 1968) in which flow passes from subcontrol flow (upstream) to supercontrol flow (slightly below the measurement point). This point controls the water level directly above it and is not influenced by flow immediately downstream. V-notch weirs and similar devices are inserted in small streams to create these conditions (Scheider et al., 1983) but must be kept free of ice and debris. In large streams, such weirs are impractical, but judicious selection of a natural constriction gives some of the same flow characteristics.

Accuracy of Streamflow Records

The validity of streamflow data is difficult to assess since site-specific conditions, control, method of observation and frequency of measurement can and do vary between gauge sites (including multiple sites on the same stream system). As noted above, where control is good, a continuous recorder should yield water level data that are accurate to within 5% of the true value (P.I. Campbell, verbal communication, 1984). Personnel with the Saskatchewan and Ontario Environment ministries have suggested that an accuracy level of 10% to 15% would be appropriate for discharge measurements. Where control is poor and measurement infrequent the overall error could reach 50% (P.I. Campbell, verbal communication, 1984). More reliable, site-specific estimates can be obtained from Environment Canada and the relevant Provincial agencies.

APPENDIX 1

Historical Review of Methods Used for the Analysis of Radioactive Ores at the Mines Branch

I. ANALYTICAL METHODS FOR URANIUM DETERMINATION

A. Ores

The chemical methods used prior to 1947 are listed below. The reported precisions as relative standard deviations are generally less than ±5%.

I.1 Arsenic volatilization, hydrogen sulphide separation, ammonium carbonate separation, gravimetric finish:

a) method used at Port Radium prior to 1948;
b) lower limit probably 2% (careful work);
c) precision: unknown, but the standard deviation was probably around ± 5% at the high levels in this ore;
d) reference: Rodden and Furman, 1946.

I.2 Arsenic volatilization, hydrogen sulphide separation, cupferron separation, volumetric dichromate finish:

a) method used at Bureau of Mines (Canada) 1947;
b) lower limit - 2%;
c) precision:

Concentration Level	Relative Standard Deviation (estimate)
0.1%	± 10-15%
1.0%	± 3-5%
5.0% and up	± 0.5%

d) references: Anon, 1947; Rodden and Tregoning, 1950 (Method 1).

I.3 Mercury cathode-cupferron separation volumetric dichromate finish:

a) method used at Mines Branch, 1947-1949;
b) lower limit of determination: 1.0%;
c) precision:

Concentration Level	% Relative Standard Deviation
0.1%	± 10-15%
1.0%	± 3-5%
5.0% and up	± 0.5%

d) reference: Rabbits, 1949a; Rodden and Tregoning, 1950 (Method 3).

I.4 Cellulose column separation with volumetric finish:

a) method used at Mines Branch, 1949-1951;
b) lower limit of determination: 1.0%;
c) precision:

Concentration Level	% Relative Standard Deviation
0.1%	± 10-15%
1.0%	± 3-5%
5.0% and up	± 0.5%

d) reference: Rabbits, 1949b, 1952; Burstall and Williams, 1950.

I.5 Cellulose column separation with colorimetric peroxide finish:

a) method used at Mines Branch, 1949-1952;
b) lower limit of determination: 0.001%;
c) precision:

Concentration Level	% Relative Standard Deviation
0.1% and up	± 0.5%

d) reference: Rabbits 1949b, 1952.

I.6 Ethyl acetate separation with colorimetric peroxide finish; direct acid differential versions:

a) method used at Mines Branch, 1952 onward;
b) lower limit of determination: not used routinely for ores containing less than 5% U_3O_8;

c) precision:

Concentration Level	% Relative Standard Deviation
direct 5% and up	± 0.25%
differential 25% and up	± 0.04%

d) reference: Ingles, 1959.

I.7 Fluorimetric method - MIT Model 3 fluorimeters

a) method used at Mines Branch, 1950 onward;

b) lower limit of determination: 0.0025% - the method was used routinely for all samples containing less than 1% U_3O_8, which included most of the ores encountered;

c) precision: using Mohr pipettes (1950 to about 1953):

Concentration Level	% Relative Standard Deviation*
0.01%	± 3.5%
0.1%	± 2.2%
1.0%	± 1.7%

using micropipettes (1953 onward):

Concentration Level	% Relative Standard Deviation*
0.5%	± 1.5%

*Standard deviation for the average of two beads on a plate of 22, including four standards and two blanks. When desired, the values for the relative standard deviation could be approximately halved by running two samples (8 beads each) to a plate, or reduced by a factor of about 2.5 by running a whole plate of 16 beads per sample.

Other alterations in the method included the use of preformed tablets, platinum alloy dishes (iridium alloy and later gold alloy), between 1953 and 1958, and the introduction of a rotating head gas burner (1971).

d) reference: Ingles, 1959.

In a study done around 1973, however, the following precision data were observed:

Concentration Level	% Relative Standard Deviation
0.0046%	± 2.8%
0.023%	± 3.6%
0.177%	± 3.7%
0.183%	± 3.3%
0.451%	± 2.1%

reference: Ingles et al., 1977.

These were whole plate values.

Precision Data

Data representing uranium analyses that were conducted on samples exchanged among a number of laboratories display relatively good agreement. The results of sample exchanges are presented below. The relative differences among results from these laboratories, based on these samples, were generally less than ±10%. These samples represent ores and tails from a number of locations in Canada.

Results of Sample Exchanges (% U)

Blind River, 1958:

	Denison	Stanrock	Stanleigh	Mines Branch
Ores (Denison ore samples)				
	0.126	0.128	0.132	-
	0.124	0.126	0.118	-
	0.068	0.078	0.073	0.075
	0.079	0.078	0.078	0.085
	0.085	0.079	0.080	-
	0.075	0.082	0.075	-
	0.075	0.080	0.077	-
	0.079	0.082	0.074	-

Reference: Mayling, 1960.

Leach Tails (1958) (Denison leach residues):

Denison	Stanrock	Stanleigh	Mines Branch
0.0068	0.0068	0.0065	-
0.0064	0.0062	0.0063	-
0.0061	0.0065	0.0062	0.0070
0.0062	0.0075	0.0067	0.0080
0.0072	0.0076	0.0072	-
0.0042	0.0050	0.0034	-
0.0044	0.0044	0.0033	-
0.0048	0.0060	0.0046	0.0070

Reference: Mayling, 1960.

Beaverlodge, 1960

Ore (monthly composites): Beaverlodge

Beaverlodge	Eldorado Ottawa	Eldorado Port Hope	Mines Branch
0.212	0.217	0.213	0.22
0.212	0.202	0.208	0.20
0.208	0.208	0.212	0.21
0.216	0.228	0.222	0.23
0.204	0.201	0.210	-

Tails (monthly composite): Beaverlodge leach residues:

Beaverlodge	Eldorado Ottawa	Eldorado Port Hope	Mines Branch
0.018	0.0182	0.0186	0.021
0.017	0.0176	0.0166	0.017
0.021	0.0215	0.0214	0.022
0.017	0.0188	0.0182	0.020
0.020	0.0196	0.0206	-
*0.0176	0.0181	0.0191	0.0185

*Cooperative precision test

Cooperative Precision Test, Beaverlodge Tails:

	Mines Branch	Beaverlodge	Port Hope*	Eldorado R&D
Analyses	20	19	20	100
Mean	0.0185	0.0176	0.0191	0.0181
Standard Deviation	0.00122	0.00218	0.00076	0.00125
% Relative Standard Deviation	± 6.6%	± 16%	± 5.0%	± 6.9%

*Port Hope x-ray Method.

Reference: Smart, 1960.

Precision of fluorimetric uranium determinations at Dyno Mines Ltd., Bancroft, Ontario in 1960 (based on a suite of 12 analyses performed on successive days). Each analysis is the average of four determinations.

Concentration Level	% Relative Standard Deviation
Ore: 0.062%	± 3.3%
Tails: 0.002%	± 11.6%

Analyses were also checked by the ethyl acetate colorimetric method.

Reference: Saari, 1960.

B. Residues and Tailings

Prior to 1950, the methods for leach residues were the same as for ores, except that larger samples (up to 25 grams) were taken, usually distributed initially over several beakers, then after dissolution and the initial separations, they were combined.

Methods used after 1950 are listed below, and generally have precisions of ±1 to 2%.

I.7 Fluorometric method (see I.7 above).

I.8 Tributyl phosphate - ethyl acetate separation - colorimetric peroxide or thiocyanate separation:

a) method used occasionally after 1954 with an extra large sample, to check fluorimetric results;

b) lower limit: 0.01% (peroxide)
0.005% (thiocyanate)

c) precision:

Concentration Level	% Relative Standard Deviation
Peroxide finish: 0.01%	2.5% (2 gram sample)
Thiocyanate finish: 0.005%	2.5% (2 gram sample)

d) reference: Ingles, 1959.

I.9 Tri-n-octyl phosphine oxide (TOPO) extraction separation, colorimetric (bromo PADAP) finish:

a) used occasionally after 1970 in the certification of reference standards of uranium ores and tails;

b) lower limit: 0.0005%;

c) precision:

Concentration Level	% Relative Standard Deviation
0.005%	1%

d) reference: Ashbrook, 1971.

I.10 X-ray emission determination:

a) used occasionally beginning about 1965 - used to supplement fluorimetry after 1974;

b) lower limit: no information;

c) precision: no information;

d) reference: Zimmerman and Reynolds, 1974.

II. ANALYTICAL METHODS FOR THORIUM DETERMINATION

During the period prior to 1952, most of the ores analyzed were complex - niobium and tantalum - titanium ores requiring numerous separations. Precision was probably never better than ±10% relative standard deviation, and often worse.

The methods in use prior to 1950 are listed below.

II.1 Mercury cathode separation, potassium iodate separation - oxalate precipitation gravimetric finish:

a) period of use: 1947-48
b) lower limit: 2%
c) precision: see note below
d) reference: Rabbits, 1947 (unpublished)

II.2 Oxalate separation - hexamine separation - oxalate precipitation - gravimetric finish:

a) period of use: 1947-48
b) lower limit: 2%
c) precision: see note below
d) references: Chase, 1948 (unpublished), similar to Rodden and Tregoning, 1950 (Method 7); Rodden and Furman, 1946

II.3 Cellulose - ether column separation (using 12.5% nitric acid in ether) - oxalate separation - gravimetric finish. (If the amount present was less than 0.1%, lanthanum was used as a carrier and the determination was completed spectrographically.):

a) period of use: 1950-1951 - discontinued because it represented a fire and safety hazard
b) lower limit: probably 0.005%
c) precision: see note below
d) references: Hunt, Smith and Williams, 1950; Hunt, Kingsbury and Williams, 1951; Radioactivity Division, 1950 (unpublished); Ryan, Hunt, Smith and Wells, 1963.

II.4 Methyl oxalate separation - mesityl oxide extraction - colorimetric "Thorin" finish:

a) period of use (with modifications): 1951 onward
b) lower limit: 0.001% (2 gram sample)
c) precision: see note below
d) reference: Ingles, 1951, 1959

II.5 Sebacic acid separation - mesityl oxide extraction - colorimetric "Thorin" finish:

a) period of use: 1956 onward
b) lower limit: 0.001% (2 gram sample)
c) precision: see note below
d) reference: Ingles, 1959

II.6 Radiometric emanation method (ores only):

a) period of use: 1955 onward
b) lower limit: 0.01% (10 gram sample)
c) precision: see note below
d) reference: Zimmerman and Bouvier, 1955; Ingles, 1959.

II.7 Modified "Thorin" colorimetric method (modification applicable to methods B4 and B5):

a) period of use: 1959 onward
b) lower limit: 0.001% (2 gram sample)
c) precision: see note below
d) reference: Bouvier and Guest, 1958

II.8 Cation exchange in 4 M hydrochloric acid followed by elution with 4 M sulphuric acid, colorimetric "Thorin" finish:

a) period of use: 1965 onward
b) lower limit: 0.001% (2 gram sample)
c) precision:

Concentration Level	% Relative Standard Deviation
0.001%	± 3.5 to 8.9%
0.008%	± 2.24%
0.11%	± 1.15%

d) reference: Chung and Riley, 1963; Barkley and Bouvier, 1974; Ingles et al., 1977

II.9 TTA solvent extraction, fluoride separation, colorimetric "Thorin" finish:

a) method used at Rio Algom Mines Ltd.
b) lower limit: unknown
c) precision: unknown
d) reference: National Lead Co., 1958; Fisher, 1974.

II.10 Lanthanum hydroxide carries precipitation separation, colorimetric "Thorin" finish:

a) method used at Denison Mine Ltd., 1959
b) lower limit: unknown
c) precision: unknown
d) reference: Brooks, 1959

From 1952 onward, complex ores continued to be analyzed, probably with little improvement in precision. However, none of the properties sampled ever resulted in the development of mines.

For Elliot Lake ores, there are few data. Routine analyses would probably have had relative standard deviations between ± 5 and 10%.

Some methods (e.g., II..9 and II.10) were mainly used for determining thorium in concentrates for specification purposes, but one method (II.9) was probably a good method for both ores and residues.

III. ANALYTICAL METHOD FOR RADIUM DETERMINATION

Only one method was used for analysis of radium. The precision of this method, which is listed below, is generally on the order of about ± 5%.

III.1 Coprecipitation on mixed barium and lead sulphates, lead removal, alpha spectrometry:

a) method used from 1975 on
b) lower limit: 2 pCi
c) precision:

Concentration Level (pCi)	% Relative Standard Deviation
5	12%
150	3%
1,000	2%

d) reference: Zimmerman and Armstrong, 1975.

IV. ANALYTICAL METHODS FOR NON-RADIOACTIVE ELEMENT DETERMINATION

Analytical methods for non-radioactive element determination are discussed in a general way in the introduction of Section 3.1.1. The methods themselves are listed below and are detailed in Canadian Mineral Analysts (1972, 1974), Robson (1950), Ingles (1950). Much less information is available on precision of the methods of interest, and locating it would be much more time-consuming (Ingles, personal communication). Typical detection limits also vary greatly among elements.

Element	Method	Detection Limit
Zr	Gravimetric (using Mandelic acid/ oxides)	10-300 mg ± 5%
Al	Fluorimetric (with 8-hydroxyquinoline)	0.0005%
As	Distillation-Branatometric (weak titrant)	0.01%
	(colorimetric finish)	0.001%

Element	Method	Detection Limit
B	Colorimetric	0.001%
Bi (oxychloride)	Gravimetric	2-200 mg
Ca (oxide)	Volumetric oxalate	0.0005-0.1 gm
Cl	Volumetric	0.03% in precipitate
		0.003 gm/L in solution
Co	Colorimetric	0.05% (gm/L)
Cu	Gravimetric by electrodeposition	0.005-5 gm ± 0.1%
	Colorimetric (with Cuproine)	0.001%
	Volumetric iodide	0.005-0.25 gm ± 1%
F (fluosilicic acid)	Volumetric	0.001%
Fe	Colorimetric	0.005% (gm/L)
	Volumetric	5-150 mg ± 0.2%
	Ethyl acetate extraction -	
	Colorimetric -	0.001-0.1 gm/L solution
	Bathophenathroline finish	0.001-0.1% solid
Hg	Distillation - titration	5-500 mg in 2 gm ± 0.3-1 mg
Mg (pyrophosphate)	Gravimetric	0.0005-0.2 gm
Mn (permanganate)	Colorimetric	0.02% (gm/L)
Mo		0.0001%
Nb (Nb_2O_5)	Colorimetric (thyocyanate/ether ext.)	0.03%
Ni	Gravimetric	0.001 gm-0.1 gm
Si	Gravimetric	0.5-2% ± 5%
Ti	Colorimetric (with ascorbic acid)	0.005%
V	Colorimetric (peroxide)	0.25%
Zr	Gravimetric (using mandelic acid/ oxides)	10-300 mg ± 5%

APPENDIX 2

Questionnaire Administered to Participating Analytical Laboratories

QUESTIONNAIRE FOR EVALUATION OF ANALYTICAL LABORATORY SERVICES

Name of Laboratory:

Address:

Telephone:

Laboratory Manager:

Date/Year Established:

Clients: % type of industry; % government; % other (specify)

CHRONOLOGY OF ANALYTICAL SERVICES

For each subject heading below, please describe original analytical services at the time of laboratory establishment, changes in service and approximate date of changes, and current services. Attach pages as required.

Radionuclide and Metal Analyses

List of Radionuclide Parameters:

List of Metal Parameters:

Reference(s) for Analytical Methods (and parameters to which applied):

Any Modification(s) to Methodology (describe or attach typed protocol):

Instrumentation Available (model and date acquired):

Precision and Detection Limits for Each Parameter:

Formal Qualifications and Training for Analytical Technicians and Supervisors (give range):

Average Volume of Analyses (per month or year):

Quality Assurance (Please describe past and present)

Internal Quality Control (e.g., replicate analyses, spiking, blanks, reference material)(frequency)

Interlaboratory Comparisons (frequency):

Overall Quality Assurance (percent of working time, general rating):

Sample Handling Methods (by parameter and sample type if appropriate)

Sample Collection Personnel (instructions, training, standardization):

Sample Containers (based on sample matrix, i.e., glass, polyethylene, plastic bags):

Sample Treatment (e.g., filtration, subsampling):

Sample Preservation (e.g., acidification, freezing):

Sample Transportation and Storage (time lag prior to analyses):

Data Reporting Protocol (proofing; checking calculations; computerization):

APPENDIX 3

Revised Criteria for Data Quality Evaluation

CRITERION REPRESENTING ANALYTICAL METHODOLOGY

Component		Points
A.	Lab uses externally documented methods (i.e., subjected to critical peer review and published in open literature)	15
	OR	
	Uses internally documented methods (i.e., not published, but open to inspection on request)	3
	OR	
	Uses internal methods not open to inspection	0
B.	Lab involved in developing (publishing) new methods	3
	OR	
	Not involved in methods development	0
C.	Highest level of education: Ph.D.	3
	OR	
	M.Sc.	2
	OR	
	B.Sc./Technical Diploma	1
D.	Successful performance in recent officially recognized inter-laboratory comparison such as CANMET (degree of internal precision, relative to other participants)	0-4
	OR	
	Successful participation in other formal interlaboratory exchange studies	2
	OR	
	Successful participation in "umpire" programs	1
	OR	
	No comparison with other labs or poor performance	0

Composite point score (A-D) = sum of points, normalized against the maximum possible and converted to a 0-9 scale.

CRITERION REPRESENTING ANALYTICAL QUALITY CONTROL

Component		Points
A.	Report proofing for transcription errors:	
	double	10
	single	5
	none	0
B.	Checking (i.e., reworking) intermediate calculations:	
	all calculations checked	5
	spot checking	3
	no checking	0
C.	Logical checks by computation (e.g., statistical outliers, mass balance, ion balance, etc.):	
	performed in all applicable cases	10
	performed in some cases	5
	not performed	0
D.	Time devoted to quality assurance (% of total man-hours, normalized against a maximum of 15%, i.e., percentages ≥15 result in the highest score of 10)	0-10
E.	Routine use of replicates, standards and blanks:	
	All above used routinely (every batch of samples)	10
	Some of above used routinely	5
	None of above used routinely	0
F.	Number of interlaboratory studies per year (normalized against a maximum of five studies per year, i.e., frequencies ≥5 result in the highest score of 10)	0-10
	OR	
	Routine submission of duplicates to another reputable lab (entire "umpire" program considered equal to a single formal interlaboratory study)	2

Composite point score (A-F) = sum of points, normalized against the maximum possible and converted to a 0-9 scale.

CRITERION REPRESENTING SAMPLING METHODOLOGY

Component	Points
Sample Collection and Identification	
A. Sample type (phase, matrix, etc.):	
Documentation adequate	1
Documentation inadequate	0
B. Location (position, depth, etc.):	
Documentation adequate	1
Documentation inadequate	0
C. Collection methods (equipment, flushing, etc.):	
Documentation adequate	1
Documentation inadequate	0
D. Chain of sample custody (individual responsible, sample number, etc.):	
Documentation adequate	1
Documentation inadequate	0
E. Sampling staff qualifications:	
Technical or professional	1
No formal credentials	0
Not stated	0
Treatment Methods	
F. Sample preservation (acidification, refrigeration, etc.):	
Documentation adequate	1
Documentation inadequate	0
Documentation inapplicable	1
G. Sample filtering (pore size, etc.):	
Documentation adequate	1
Documentation inadequate	0
Documentation inapplicable	1

H. Sample storage (time, conditions, etc.):

Documentation adequate	1
Documentation inadequate	0

Field Analysis

I.	pH, Eh:	Documentation adequate	1
		Documentation inadequate	0
		Documentation inapplicable	1
J.	Specific conductivity:	Documentation adequate	1
		Documentation inadequate	0
		Documentation inapplicable	1
K.	Temperature:	Documentation adequate	1
		Documentation inadequate	0
L.	Dissolved oxygen:	Documentation adequate	1
		Documentation inadequate	0
		Documentation inapplicable	1
M.	Stream flow:	Documentation adequate	1
		Documentation inadequate	0
		Documentation inapplicable	1

Composite point score (A-M) = sum of points, normalized against the maximum possible and converted to a 0-9 scale.

CRITERION REPRESENTING CONTINUITY OF THE SAMPLING OR FIELD MONITORING PROGRAM

Component	Points
A. Total number of measurements for a particular parameter at a particular location (relative to a required number considered adequate for characterization of the probability density function; required replication proportional to expected variability; all measurements in a set receive the same score):	
100% of required replication	3
≥ 50% of required replication	2
≥ 10% of required replication	1
< 10% of required replication	0

APPENDIX 4

Peer Review of Criteria

ACRES

RECEIVED
DEC 07 1984

December 4, 1984

IEC Beak Consultants Ltd.
6870 Gorway Drive
Mississauga, Ontario
L4V 1P1

Attention: Dr. Ronald R. Hart

Gentlemen:

This letter is in response to your solicitation for comments for CAMUT data evaluation. In general, your system appears to be quite suitable; however, in the attachment, our comments are itemized according to the sections and subsections provided.

Please note that Acres received two copies of your request; one addressed to Ms. Leslie Smythe (environmental department), and one addressed to Mr. Ryan Ellis (laboratory department). To avoid confusion, future correspondence in this respect can be sent directly to me as I am the coordinator for Acres analytical laboratory.

We appreciate the opportunity to participate in your study. If you have any further requirements, please do not hesitate to call me.

Yours very truly,

A. W. Panko, Ph.D
Environmental Scientist

AWP:amh

Encl

ACRES CONSULTING SERVICES LIMITED
5259 Dorchester Road, P.O. Box 1001, Niagara Falls, Ontario L2E 6W1
Telephone 416-354-3831 Telex 061-5107
Cables ACRESCAN NFS

Toronto, Burlington, Calgary, Halifax, Niagara Falls, St. John's, Vancouver, Winnipeg

Analytical Methodology

Component A - High points (15) for externally documented methods make sense. Most laboratories (ours included) almost exclusively use Environment Canada Methods Manual or Standard Methods.

Component B - Laboratories with high throughputs and small capital, or very small laboratories, may not have the funds to be part of the leading edge in methods development, although I suspect it is true that this type of progressive work reflects on all aspects of the laboratories operations.

Component C - No comment.

Component D - This is a good point. We have participated in several Environment Canada programs, as well as some we have initiated ourselves. A problem I see here is that smaller laboratories may not always be included when these programs are set up.

Quality Control

Component A - Double proofing is a lot easier now since with computerized systems, only one or two transcriptions take place.

Component B - In laboratories working calculations by hand, checking all calculations is necessary, but in laboratories like ours, where almost all calculations are performed by computer, only spot checks are conducted. We would, therefore, lose two points for using a computerized system.

Component C - No comment.

Component D - Very good.

Component E - Perfect.

Component F - Our laboratory is only notified of one or two interlaboratory studies per year and are of course, limited to participation in those programs for which we have expertise. For example, we do not have GC/MS facilities and, therefore, must pass on any studies involving organics, although we may have capability in other components of that program.

Sampling Methodology

Components A - M - Our laboratory generally "follows the book" in field sampling and analysis. In unique or exceptional cases where this is not possible, the client and/or government agency is asked to approve any deviations from accepted procedures.

Continuity of Sampling

Component A - No comment.

Atomic Energy of Canada Limited
Research Company
Chalk River Nuclear Laboratories

L'Énergie Atomique du Canada, Limitée
Société de Recherche
Laboratoires Nucléaires de Chalk River

Chalk River, Ontario
Canada K0J 1J0
Telephone: 613-584-3311
Telex: 053-34555
Cable Address: "MOTA"
Telecopier: 613-589-2039

Health Sciences Division
Environmental Research Branch

1984 November 29

Dr. Donald R. Hart
Applied Ecologist
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

CANUT DATA BASE CRITERIA

The proposed criteria deal, in general, with the kind of information required to evaluate data from analytical laboratories but some component weightings seem out of proportion. As an example, in the Analytical Methodology section too many points are given to component A (15) and not enough to B (3) and D (0-4). Involvement in analytical R&D, as component B requires to achieve maximum score, plays an important role in maintaining both interest in and competency of analysis. The 15 points allotted to component A could be earned by a laboratory involved in simple routine analysis with no R&D interest. There should be some distinction made here. Also successful performance in interlaboratory studies, that could earn up to 4 points as the scoring now stands, is a powerful assurance that all is well with the analytical method. In fact collaborative testing should be an essential pre-requisite for any analytical method used in environmental impact studies. I would suggest that maximum points in these components be distributed as follows: A - 10; B - 5; C - 3; D -5. This would mean that B+D points would equal those earned by A. This seems more balanced and reasonable.

Point allocation to components in the Analytical Quality Control criterion are also out of balance, e.g. B (checking calculations) should be equally weighted with A (report proofing). What is the point in checking for transcription errors if the calculations themselves are incorrect?

The Sample Methodology criterion components are mostly scored as "adequate or inadequate". This seems highly subjective. What is adequate? This whole criteria would be better if the exact component requirements were specified and scored accordingly. Such a detailed specification would need to be undertaken by those who have familiarity with environmental sampling as there are many factors to be taken into account. We may be able to assist if such a revision is undertaken.

The last criterion, Continuity of the Sampling or Field Monitoring Programs is unclear. Presumably the intention is to evaluate whether the samples are representative or not. This is a statistical problem and should be defined in a statistical manner. As the criterion stands at present it is difficult to be certain what is being scored.

I enclose a xerox of "Principles of Environmental Analysis", by Keith, L.H. et al., published in Analytical Chemistry 1983, 55, 2210-2218. You may already have seen it but if you haven't it deals closely with the matter the CANUT database criteria covers.

Sincerely,

J.M. Judd

JMJ/es
Encl.
c.c. D.R. Champ
R.V. Osborne
W.A. Seddon

Atomic Energy of Canada Limited
Research Company

Whiteshell Nuclear Research Establishment

L'Énergie Atomique du Canada, Limitée
Société de Recherche

Etablissement de Recherches Nucléaires de Whiteshell

Pinawa
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Canada
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Telex 07-57553
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SLI-84-43
1984 December 6

Dr. Donald R. Hart
Applied Ecologist
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
Canada L4V 1P1

RECEIVED
DEC 12 1984

Dear Don:

I have examined the proposed criteria for evaluation of analytical and sampling methodology for the National Uranium tailings program data base as you asked and have the following comments.

Analytical Methodology

1. The intent appears to be to apply a single "figure of merit" to all analyses coming from a laboratory. Many labs do a wide range of analyses some types of which may be fully documented and externally compared while others are not. The lab may perform well on one type of analysis and poorly on another. You may get better results by assigning the figure of merit based on both the type of analysis and the identity of the lab.

2. In part D, "officially recognized" by whom?

Sampling Methodology

3. Points could be given for routine collection and storage of replicate or sub-samples. These can be discarded after lab and data analysis is completed if no anomalies are found.

4. The words "Documentation inapplicable" should be replaced with "procedure not required" or similar.

5. Points could be given for labs having documented procedures for calibration and accuracy checking of meters and other instruments, particularly procedures carried out in the field under the same conditions the measurements are made.

Continuity of Sampling

6. Rewrite as follows ".....location (relative to the number considered adequate to characterize the probability density function considering the expected variation). All measurements....".

7. Replace "required replication" with "required number of samples".

.../2

In general the criteria look reasonable and it will be interesting to learn if they are correlated with error rates you observe in data sets. I would be interested in learning the results of your study and receiving a copy of the criteria after they are finalized.

Sincerely

S. L. Iverson

S.L. Iverson
Environmental Research Branch

bb

Atomic Energy Control Board
Commission de contrôle de l'énergie atomique

P.O. Box 1046
Ottawa, Canada
K1P 5S9

C.P. 1046
Ottawa, Canada
K1P 5S9

DIRECTORATE OF FUEL CYCLE
AND MATERIALS REGULATION

Telephone: (613) 593-5123

Your file Votre référence

Our file Notre référence

December 3, 1984

37-19-1-0
34-5-7-0

Dr. Donald R. Hart
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Sir:

Your letter of 84/11/15 has been passed to me for a reply. As I was a member of the working group that helped set up the criteria some weeks ago, I am not sure that I am justified in commenting on them now. However, I have already been asked for comments by Roy John, and I enclose a copy of my letter to him. You are of course free to apply any weighting factor that you feel is appropriate.

Yours sincerely,

R.A. Washington
Technical Advisor
Compliance Services and
Laboratories Division

cc: B. Zgola

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DEC 11 1984

Canada

Atomic Energy Control Board
Commission de contrôle de l'énergie atomique

P.O. Box 1046
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DIRECTORATE OF FUEL CYCLE
AND MATERIALS REGULATION

Telephone: (613) 993-5123

Your file / Votre référence

Our file / Notre référence

13 November 1984

37-19-1-0
34-5-7-0

Dr. Roy John
Dept. of Energy, Mines and
Resources
Canada Centre for Mineral
and Energy Technology
National Uranium Tailings
Programme
560 Rochester Street
Ottawa, Ontario
K1A 0G1

Dear Roy:

As requested, I have reviewed the enclosed summary of the proposed criteria for evaluation of the CANUT data base.

I can offer no serious criticism of the scoring system, although (as I indicated at the recent meeting on the subject) I might personally be inclined to assign slightly different weights to some of the factors, and to rate on an overall scale of 0 to 5 rather than 0 to 9, as I cannot convince myself that ratings which are largely subjective can really be sliced so thinly.

I am slightly confused by one point, though. In the "Field Analysis" component of the "Sampling Methodology" criterion, a rating of 1 is assigned to "inapplicable" documentation. Should this not be 0? It appears that "inapplicable" documentation is being rated at the same level as "adequate" documentation, rather than at the same level as inadequate".

Your very truly,

R.A. Washington
Compliance Services and
Laboratories Division

RAW:gc

Canada

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TELEPHONE 984-0221
AREA CODE 604
TELEX 043-52597

ANALYTICAL CHEMISTS
GEOCHEMISTS
REGISTERED ASSAYERS

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NOV 30 1984

CHEMEX LABS LTD.

November 27, 1984

Dr. Donald Hart
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ont.
L4V 1P1

Dear Dr. Hart:

Thank you for your summary of proposed criteria for evaluation of data for the National Uranium Tailings Program. We have reviewed the document and have a number of comments. In general the criteria seem reasonable and if applied equally to all laboratories should be acceptable to all. One potential problem that may occur regards verification of information submitted by laboratories with respect to for example quality control items such as proofing, checking, use of replicates, blanks and standards. Obviously most laboratories would claim this is done but it is very difficult to prove it. For this reason we would prefer that the points awarded for successful participation in interlaboratory comparison studies be significantly increased as this is one of the few instances in which a clear evaluation of a laboratory can be obtained, particularly with respect to proofing, computational checks, bias etc.

We note also that a significant number of points have been assigned to logical checks by computation. In our experience, the performance of these checks has always depended upon whether the client has authorized sufficient analyses to permit these calculations, and not whether we were inclined to perform them.

I trust this information will be of some use to you.

Yours sincerely,

Micheal LeGeyt
Project Supervisor

MLG/gr

CLUFF MINING

817 - 825 45th STREET WEST, P.O. BOX 9204, SASKATOON, SASKATCHEWAN S7K 3X5

RECEIVED
JAN 03 1985

December 21, 1984

Dr. Donald R. Hart
IEC Beak Consultants Ltd
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

This is in response to your recent letter and proposed criteria for evaluation of data in the CANUT data base related to NUTP.

On the criterion representing Analytical Methodology, my opinion is that the use of externally published methods is overemphasized. All methods are generally published but may not be exactly as published. In addition, externally documented methods generally have to be adjusted or modified to accommodate specific sample conditions of a particular operation.

Regarding section F under criterion representing Analytical Quality Control, the necessity for interlaboratory studies varies with the nature of the laboratories. For example, laboratories that routinely handle the same types of samples. once they are certain of the accuracy of their analyses, then there is no further need for interlaboratory studies. Hence, I think this point cannot be generalized for all laboratories.

Under criterion representing Analytical Quality Control, my suggestion is to consider including this addition, "Routine use of internal comparison of results by two or mor analysts."

On criterion representing Sampling Methodology, my comment is that too low an emphasis is given to sampling since the analysis is only as good as the sample. Under this section. considerations should be given to sampling methods such as automatic versus manual sampling and sampling frequency.

The above are my thoughts regarding your proposed criteria. If I can help further in this matter, please contact me.

Yours sincerely,

Chi Lee
Chemist

CL/am

TELEPHONE: (306) 242-8804 OR 498-2233 (CLUFF LAKE) TELEX: 274-2808

Eldorado Resources Limited
Suite 400, 255 Albert Street
Ottawa, Ont. Canada K1P 6A9
(613) 238-5222 Telex: 053-3382

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DEC 03 1984

eldorado

27 November 1984

Dr. Donald R. Hart,
Applied Ecologist,
IEC Beak Consultants,
6870 Goreway Drive,
MISSISSAUGA, Ontario
L4V 1P1

Dear Dr. Hart:

Re: Proposed Criteria for Evaluation of CANUT Database

We have the following comments on the sections relating to Analytical criteria.

Analytical Methodology

A. There is a very large spread in points between the first two choices. Perhaps an additional, intermediate choice, such as; "Internally documented methods based on (and referenced to) published literature" could be used and assigned a point value of 10.

C. Along with level of education, some point value should be awarded for staff experience.

D. This component surely relates to Analytical Quality Control.

Analytical Quality Control

Components A and B could be amalgamated. F could be combined with D (Analytical Methodology) and used as a measure of accuracy.

Our main concern would be that a laboratory might obtain a relatively high rating by using externally documented methods, being involved in method development, and having Ph.D's on staff, yet fail to produce accurate results. Your suggested "dry run" using trial data evaluations will hopefully point out such inconsistencies.

Hope that the above comments are of some use to you.

Yours very truly,

G.T. Day, Superintendent,
Analytical Services,
Research & Development

0939K

Eldorado Resources Limited
Suite 400, 255 Albert Street
Ottawa, Ont. Canada K1P 6A9
(613) 238-5222 Telex: 053-3382

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17 December 1984

Your ref. 2246.1

Dr. Donald R. Hart
Applied Ecologist
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

RE: PROPOSED CRITERIA FOR EVALUATION OF CANUT DATABASE

Since our R&D department has previously submitted comments to you on Analytical Criteria, my comments are restricted to Sampling Methodology and Replication.

Sampling Methodology

I think you have covered most items of concern. I wonder, however, how you will obtain appropriate information on the various items from which to assign a score. Further, I would think that the procedures used by the sampler would be more important than documentation. This would apply particularly to Items C, G, I, J, K, L, and M. Items C, D, E and F are deserving of greater weighting than the others. Field Analyses should be grouped to provide a net score of 1 or 2.

Criterion Representing Continuity of the Sampling or Field Monitoring Program

I don't understand what this item refers to, except possibly duplicate sampling or duplicate analysis. How is required replication determined? Duplicate results are normally not included in the databases which you are evaluating, to my knowledge.

.../2

I hope these comments are of some use to you.

Yours very truly

M.P. Filion, P.Eng.
Environment and Technology

/as

ENVIROCLEAN
A DIVISION OF MacLAREN PLANSEARCH INC.
320 Adelaide Street South, London, Ontario N5Z 3L2 (519) 686-7558

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DEC 03 1984
IEC BEAK

35342-1019

29 November 1984

Dr. Donald J. Hart
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

In response to your letter I offer the following comments regarding the proposed criteria for evaluation of the CANUT Database. I have confined my remarks to those areas with which we as a laboratory are concerned routinely, Analytical Methodology and Analytical Quality Control.

The proposed criteria cover all of the essential points but the scoring seems to under-emphasize measures of routine laboratory performance. For example, according to the proposed scoring, a laboratory using staff with significant paper qualifications and officially recognized methods could score high marks but still produce biased or erratic analytical results. The criterion of research activity in analytical methods development is not necessarily relevant to a laboratory's ability to perform routine analyses. Measures of data quality should give a stronger emphasis to peer challenge by participation in inter-laboratory programs and to statistical measures of routine laboratory performance. Some suggested revisions to the scoring system which would reflect this emphasis are indicated on the attached copy of the proposed criteria.

I trust you will find these comments helpful. If you would like to discuss them further please do not hesitate to call.

Yours very truly,

W. M. Neaves, M.Sc.
Chemist
Laboratory Services

1

CRITERION REPRESENTING ANALYTICAL METHODOLOGY

Component		Points
A.	Lab uses externally documented methods (i.e., subjected to critical peer review and published in open literature)	~~15~~ 5
	OR	
	Uses internally documented methods (i.e., not published, but open to inspection on request)	3
	OR	
	Uses internal methods not open to inspection	0
~~B.~~	~~Lab involved in developing (publishing) new methods~~	~~3~~
	OR	
	Not involved in methods development	0
C.	Highest level of education: Ph.D.	3
	OR	
	M.Sc.	2
	OR	
	B.Sc./Technical Diploma	1
D.	Successful performance in recent officially recognized inter-laboratory comparison such as CANMET (degree of internal precision, relative to other participants)	~~0~~ 15
	OR	
	Successful participation in other formal interlaboratory exchange studies	~~2~~ 10
	OR	
	Successful participation in "umpire" programs	+ 5
	OR	
	No comparison with other labs or poor performance	0

Composite point score (A-D) = sum of points, normalized against the maximum possible and converted to a 0-9 scale.

CRITERION REPRESENTING ANALYTICAL QUALITY CONTROL

Component		Points
A.	Report proofing for transcription errors:	
	double	~~10~~ 5
	single	~~5~~ 3
	none	0
B.	Checking (i.e., reworking) intermediate calculations:	
	all calculations checked	5
	spot checking	3
	no checking	0
C.	Logical checks by computation (e.g., statistical outliers, mass balance, ion balance, etc.):	
	performed in all applicable cases	10
	performed in some cases	5
	not performed	0
D.	Time devoted to quality assurance (% of total man-hours, normalized against a maximum of 15%, i.e., percentages ≥15 result in the highest score of 10)	~~0-10~~ 15
E.	Routine use of replicates, standards and blanks:	
	All above used routinely (every batch of samples)	10
	Some of above used routinely	5
	None of above used routinely	0
F.	Number of interlaboratory studies per year (normalized against a maximum of five studies per year, i.e., frequencies ≥5 result in the highest score of 10)	0-10
	OR	
	Routine submission of duplicates to another reputable lab (entire "umpire" program considered equal to a single formal interlaboratory study)	2
G.	Documentation of QA statistical data	0-4

Composite point score (A-F) = sum of points, normalized against the maximum possible and converted to a 0-9 scale.

Environment Canada Environnement Canada

Environmental Protection Service
221 Motherwell Building
1901 Victoria Avenue
REGINA, Saskatchewan
S4P 3R4

DEC 11 1984

Your file Votre référence

December 4, 1984

Our file Notre référence

4364-3

Dr. D. R. Hart
Ecologist
I.E.C. Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

Criteria to Evaluate CANUT Data Base

My staff reviewed your proposed evaluation method and offered the following suggestions:

1) Criterian Representing Analytical Quality Control Section E include spiked natural samples (not distilled water). These are submitted samples which are analyzed, spiked and reanalyzed and provide information about interference and accuracy on natural samples.

2) Criterian Representing Sampling Metholodogy. This should include a number of blind duplicates collected in the field. At least 10% of the samples should be duplicates. In addition a field sampling program should include reagent and container blanks.

I hope these comments are useful to you. For further explanations, please call Dr. Don Waite (306) 359-6438 of my staff.

Yours truly

John Witteman

John Witteman
Director
Saskatchewan District Office

DW/dd

Canada

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Radiation Protection Bureau
775 Brookfield Road
Ottawa, Ontario K1A 1C1

RECEIVED
JAN 02 19[illegible]

December 11, 1984

Dr. Donald R. Hart,
Environmental Biologist
IEC Beak Consultants Limited
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

Enclosed please find comments on the proposed criteria for the evaluation of the CANUT database prepared by Dr. R.S. Eaton and a general summary of our analytical capabilities at the present time. We are not able to provide much information on the data from Appendix C "Water Quality Data", of Volume 2, Environmental Assessment of the Proposed Elliot Lake Uranium Mines Expansion, February 1978. These were special analyses which were not conducted routinely. The information we have is attached.

I hope you find the information useful.

Sincerely,

D.P. Meyerhof
Chief
Environmental Radiation
Hazards Division

DPM/tl

Canada

Comments on the proposed criteria for the evaluation of the CANUT database:

CRITERION REPRESENTING ANALYTICAL METHODOLOGY

COMPONENT

A - Second alternative on internally documented methods. We would propose that you increase the point of value of this alternative to, say 6. Such a low value relative to externally documented methods would discourage innovation and the possible evolution of better techniques.

ANALYTICAL METHODOLOGY

D - We would suggest that participation in the CANMET Intercomparisons (first alt.) rate at the same level as participation in other formal interlaboratory exchange studies (second alt.)

Environmental Radiation Hazards Division
Radiation Protection Bureau
Department of National Health & Welfare

Ministry of
Natural
Resources
Ontario

77 Grenville Street
Toronto, Ontario M5S 1B3

Your file:

Our file:

1984.11.20

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NOV 23 1984

Donald R. Hart, Ph.D.
Applied Ecologist
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario

Dear Dr. Hart:

In response to your request for comment on the proposed criteria for evaluation of CANUT database materials I have the following thoughts relating to the analytical criteria.

First, with respect to Methodology. The use of a documented method appears to be overly rated. For example a laboratory with no qualified staff, performing no methods development work, and participating in no certification programs yet using an externally documented method, whether suitable or not, receives more points than a laboratory that has modified a published method so as to be suitable for the application in hand and is using Ph.D. staff who develop methods and participate successfully in certification programs.

The key element should surely be a method that is proven to work for the sample matrices in hand. In this laboratory we often modify published methods so as to reduce interference effects that occur in the rock samples we are asked to analyse.

Second, with respect to Quality Control. Are there not laboratories that use no transcription? If so then proof reading becomes unneccesary. Another guideline might be a demonstration that QC data were properly used to evaluate precision, accuracy and detection limit. In my experience this is often not the case and whilst it is one thing to run replicates, standards and blanks, it is quite another to know what to do with the data generated.

In all other respects I think you have done a good job in developing the criteria and hope that you will find these comments of some use.

Yours truly,

Dr. Chris Riddle, Chief Analyst
Geoscience Laboratories
Ontario Geological Survey

Environment Canada | Environnement Canada

National Water Research Institute
Canada Centre for Inland Waters
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario
L7R 4A6

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JAN 02 1985

Your file / Votre reference

Our file / Notre reference

December 26, 1984

Dr. D.R. Hart
Applied Ecologist
IEC Beak Consultants Limited
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

Attached are comments from the Analytical Methods Division on your criteria, as requested.

Yours truly,

J. Barica

J. Barica
Chief
Aquatic Ecology Division

Att.

Canada

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Government of Canada / Gouvernement du Canada

MEMORANDUM **NOTE DE SERVICE**

TO / À: Dr. J. Barica
Chief, Aquatic Ecology Division

FROM / DE: A.S.Y. Chau
Head, Quality Assurance and Methods Section

SECURITY - CLASSIFICATION - DE SÉCURITÉ
OUR FILE/NOTRE RÉFÉRENCE
YOUR FILE/VOTRE RÉFÉRENCE
DATE: December 17, 1984

SUBJECT / OBJET: Proposed critera - National Uranium
- Tailings Program

I don't know what parameters are to be analyzed in the NUTP and what substrates ....., the comments may not be specific to NUTP. (This knowledge can affect the evaluation of the proposed criteria)

(1) ANAL. Methodology - OK except that the education level of the staff has no linear relationship with quality of data generated!

It is the experience, demonstrated skill and field of expertise. In due respect of Ph.Ds or MSc., they could be worse than a BSc if they have the "wrong" experience and training.

(2) Anal. Q.C. - Components A,B,C are grossly emphasized.

Component D should have more weight

Documentation of intra and inter Q.C. results should ~~be~~ generate important points, particularly for the intra Q.C. documentation

(3)Sampling Methodology - Points given to proper documentation (A,B,C) seem a little low.

E - again, Tech. or professional does not necessarily imply sampling validity
- they should have proper training.

(4) Sampling Stategy - Don't understand the logic at all (maybe the presentation is not clear)

I have not spent too much time on this. Looks OK but the weight given to several components appear to be unbalanced. At time, the criteria are somewhat superficial.

A.S.Y. Chau

A.S.Y. Chau

Noranda Mines Limited
P.O. Box 45
Commerce Court West
Toronto, Ont., Canada M5L 1B6

noranda

(416) 867-7111

November 26, 1984

Dr. Donald Hart
Applied Ecologist
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

With reference to your letter of November 21, 1984, the proposed criteria for analytical methodology and quality control and for sampling methodology and continuity of sampling programs have been reviewed. I just have two minor observations. First, under Section D of the Criterion Representing Analytical Methodology, a laboratory can score zero points (the range is 0-4) for a "successful performance in recent officially recognized interlaboratory comparison such as CANMET" while a laboratory participating in the next two categories cannot register less than 2 or 1 point(s) respectively. Second, within the treatment and field analysis sections of the Criterion Representing Sampling Methodology, a participant registers 1 point for inapplicable documentation. I do not understand why one should be credited one point for inapplicable documentation.

Yours truly,

Hennie Veldhuizen

HV:jt

Rio Algom Limited

December 3, 1984

Dr. Donald R. Hart, Ph.D.
Applied Ecologist
IEC - Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

Re: CANUT - Database Criteria
Ref: 2246.1 D/-Nov. 21/84

Attached with this are our comments on the proposed CANUT - Database Criteria that you requested recently.

The criteria do appear practical and relevant to the context. However, we were wondering how the individual scores of the four criteria would be resolved into a single (final) value. This would be very significant when, eg., a poor score in "Sampling" could invalidate almost the whole analytical results in spite of a high score in "Methodology" or "Quality Control". We hope full consideration would be given to the final resolution of the score values.

While considering staff qualifications the importance of training and long experience, in respect to specific assays, should not be oversighted.

Also, the participation in "Umpire" programs should be well recognized as it is so appropriate, practical and significant, particularly for production oriented laboratories.

We would appreciate your comments on our preliminary views as outlined above.

With kind regards,

Biman Bihari
Process Development Dept.

BB/mp
Encl.

xc: E. Barnes
J. Nipius

CRITERION: ANALYTICAL METHODOLOGY

COMPONENT: A

Comments: This component should include additional alternatives as mentioned below:

		Points
(i)	Lab uses externally documented methods with internally developed suitable modifications; (open to inspection on request)	15
(ii)	Lab uses externally documented methods (i.e. subjected to critical peer review and published in open literature)	10
(iii)	Lab uses internally documented methods; checked with standards and by round-robin methods; but generally not open to inspection	8
(iv)	Lab uses internal documented methods (i.e. not published, but open to inspection on request)	5
(v)	Lab uses internal methods not open to inspection	0

COMPONENT: B

Comments: Under this component a Lab not involved in developing (publishing) new methods score 0 points; where as under component A it scores 15 for using externally documented methods; this appears inconsistent.

COMPONENT: C

Comments: Experience should be considered jointly with education; eg., several years of experience with a technical diploma should rank closer to a degree; if not higher.

COMPONENT: D

Comments: The first alternative should read: "successful performance in recent officially recognized inter-laboratory comparison (degree of internal precision, relative to other participants)".

Participation in "Umpire" programs should rank higher, with a range based on length of such participation.

CRITERION: ANALYTICAL QUALITY CONTROL

COMPONENT: A

Comments: A probability of transcription error due to nonproofing would generally be very small, but none the less, non-proofing is considered a poor practice for the lab. However, it should rank higher than 0 points.

COMPONENT: B

Comments: Check up of calculations is very important, however, it would prove to be too cumbersome for the Lab Supervisor/Chief Chemist to recheck all calculations. It would increase the work load excessively.

COMPONENT: F

Comments: Participation in "Umpire" program is quite significant; particularly Labs associated with production outfits where mass balances are worked out by 'head', 'tail' and 'product' components. Thus, such participation should be well recognized and merited.

The length of such participation should be merited over a range, for example, 5 to 25 years of participation should score 2 to 5 points.

CRITERION: SAMPLING METHODOLOGY

COMPONENT: (A to D)

Comments: "Adequate" - to be more specific; how this would be determined?

COMPONENT: E

Comments: Experience and training should jointly be considered, rather than just the formal qualifications.

Saskatchewan

Saskatchewan
Environment

Walter Scott Building
3085 Albert Street
Regina, Canada
S4S 0B1

File: M9-1-4-1

November 27, 1984

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DEC 0 4 1984

Donald R. Hart
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

Criteria for Evaluation of CANUT Database

I am in receipt of your letter of November 21, 1984, in which you requested review of the proposed criteria for evaluation of the CANUT database.

Mr. Ron Barsi of our Mines Pollution Control Branch,

P.O. Box 3003
Prince Albert, Saskatchewan
S6V 6G1
Telephone: (306)922-2220

is our primary representative on the NUTP Technical Advisory Committee. I have forwarded your request for comments to him and he will reply directly.

Yours sincerely,

S. L. McLeod
Resource Management Consultant
Co-ordination and Assessment Branch
Phone: (306)565-6257

SLM/ap

c.c. R. G. Barsi

Saskatchewan
Research Council 30 Campus Drive Saskatoon, Sask. Canada S7N 0X1 Phone: (306) 664-5400 Telex: SARECO 074-2484

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JAN 02 1985

December 19, 1984

Dr. D.R. Hart
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

Re: Proposed Criteria to Evaluate Data in the CANUT Data Base

Since I have not had any other involvement in this project, I find it quite difficult to evaluate this set of criteria in isolation.

The criteria for analytical methodology appear to be much better than the criteria for sampling methodology. There doesn't seem to be any evaluation of the sampling methodology other than whether or not it is documented adequately. There are certainly other aspects that are important; for example, the appropriateness of the method and equipment to the desired results, quality control, field experience of the staff, etc.. Perhaps these points are covered somewhere else.

Yours truly

Pat Tones

Patricia I. Tones
Senior Research Scientist
Environment Sector

SASKATCHEWAN RESEARCH COUNCIL

30 Campus Drive, Saskatoon, Saskatchewan, Canada S7N 0X1 Tel. (306) 664-5400 Telex 074-2484

November 26, 1984

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NOV 30 1984

IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Attention: Dr. Don Hart

Dear Don:

I have looked over the proposed rating criteria for data in the CANUT database and I'm in general agreement. The only reservations I had were on the "Criteria Representing Analytical Quality Control" and this was with respect to the relative weighting of the various components. I feel that A and C should be reduced to the same level as B (maximum of 5), thereby giving more weight to D, E and F which are probably more important in overall data reliability. Other than that I think your rating process should be quite valid in assessing relative reliability of analytical data.

Yours truly,

Gene Smithson

Gene Smithson, Ph.D.
Manager, Analytical Services Sector

GS/ldd

The Department of CIVIL ENGINEERING The University of Alberta Edmonton, Alberta, Canada, T6G2G7, telephone 432-4235

December 21, 1984

Dr. D.R. Hart
IEC Beak Consultants Ltd.
6870 Goreway Drive
MISSISSAUGA, Ontario
L4V 1P1

Dear Dr. Hart:

Please find enclosed my comments on your summary of proposed criteria for evaluation of data in the CANUT database as part of the National Uranium Tailings Program.

Yours truly

P.M. Hart

per W.B Anderson
Professional Associate

WBA/ds
Encl.

1. **CRITERION REPRESENTING ANALYTICAL METHODOLOGY**

Component

A. I agree with the use of externally documented methods and the associated weight in terms of points assigned to it (15). I feel however that labs using internally documented methods (subject to inspection) could be given more credit if method is demonstrated to be reliable through inspection, sampling program, etc. (i.e. 3-10 points).

B. This component appears to provide an opportunity for a lab to receive 'bonus' points and may not in any way represent reliability of use of existing or new methods (even if published). I feel that points should not be assigned on this basis. If necessary credit could be given in the form of a footnote.

C. Degree of education can be a factor providing that the degree of involvement in the development of analytical methodology of each person is taken into account. Weight of points should remain the same.

D. I agree with using performance in recent officially recognized interlaboratory comparison as a criterion. I feel though, that successful performance in this area reflects good analytical methodology and technique and as such should be more heavily weighted (i.e. 5-10 points).

Without a doubt far more emphasis should be placed on components A and D.

2. **CRITERION REPRESENTING ANALYTICAL QUALITY CONTROL**

Component

A. Alright as is.

B. It would be desirable to have all calculations checked but it is questionable whether any laboratories could honestly do this. Perhaps "all calculations checked" could be changed to "most calculations checked".

C. Alright as is.

D. Alright as is.

E. Alright as is with the exception of standards in the case of radium-226. Standards are used to determine cell calibration constants, which once determined, remain virtually unchanged for years. It is therefore not necessary to run standards with each batch.

F. Alright as is.

CRITERION REPRESENTING (3) SAMPLING METHODOLOGY AND (4) CONTINUITY OF THE SAMPLING PROGRAM

All components alright (field analysis not applicable in our work).

If anything more points should be assigned to this portion as sample collection, identification and treatment methods are critical to the generation of meaningful data.

THE UNIVERSITY OF CALGARY

2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

Faculty of SCIENCE
Department of PHYSICS

Telephone (403) 284-5385

1984-11-22

Dr. D.R. Hart
IEC Beak Consultants Ltd.
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Dr. Hart:

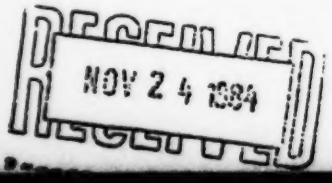
Thank you for inviting me to comment on the proposed criteria for the evaluation of data in the CANUT data base. I find it difficult to comment on the criteria outlined since I do not know how they will be utilized in the final analysis. If, let us call it, the "IEC quality factor", is to be included as a separate entry against each batch of data in the database, then I do not have any serious objection. Scientists working in the field will have a choice of using it or not; if they decide to use it as some sort of weighting factor then it would be necessary for them to explain the rational for doing so when publishing their results. Perhaps over a long period of time the "IEC quality factor" would become established as a useful parameter on the basis of established correlations.

On the other hand it is intended to delete or modify raw data in the data base using the quality factor as a criterion, I would not be in agreement. My reasons are as follows.

a) The points awarded for various components in the evaluation scheme are not derived from previous evidence. For example, has any scientist ever established that the results produced by a Ph.D. analyst are three times more precise than a B.Sc. analyst?

b) The philosophical basis of the evaluation scheme departs from accepted scientific practice. As Ziman notes:

"The general procedure is to allow all work that is apparently valid to be published; time and further research will eventually separate the true from the false" (Public Knowledge, The Social Dimension of Science. Cambridge University Press 1968).



2/-

c) Assuming that you have identified 20 or so criteria which are the sufficient number of parameters needed to predict data precision, how could such a far-reaching hypothesis ever be tested? How many laboratories would be required to yield enough degrees of freedom?

I would agree that several of your criteria require crucial questions to be answered, for example, "is the lab involved in developing new methods". The problem as I see it, is that the criteria are being applied after rather than before the work is done (indeed I see no evidence that expertise in radiometric measurements plays any role in the award of NUTP contracts). By quantifying the criteria (i.e. awarding points) you imply that a meaningful physical parameter can be derived. As ~~one~~ a scientist, such a parameter can find no application in my work and must be treated as about as reliable as rating head-ache remedies on a scale from one to ten!

Yours truly,

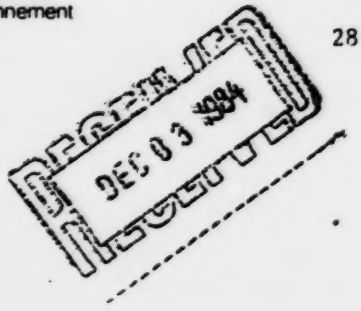
C.J. Bland
Professor of Physics

CJB/sr

Environment Canada / Environnement Canada
Environmental Protection / Protection de l'environnement

Wastewater Technology Centre,
P.O. Box 5050,
Burlington, Ontario. L7R 4A6

28 November, 1984.



Your file / Votre référence
2246.1

Our file / Notre référence
4918-1

Dr. Donald R. Hart,
Applied Ecologist,
IEC Beak Consultants Ltd.,
6870 Goreway Road,
Mississauga, Ontario.
L4V 1P1

Dear Dr. Hart:

Further to your letter to Mr. K. Conn, I would like to make the following comments on your Proposed Criteria for Evaluation of the CANUT Database:

1. I have reservations about the ability of such a scoring method to retroactively weight data in the absence of past QA programs. Method publication, high degree of education and participation in many interlab comparisons are not necessarily indicative of routine lab performance. Any correlation between the above factors and routine data quality would be loose, at best, and misrepresentative of many blocks of data, at worst.

2. You propose to correlate quality score with detectable logical inconsistencies which, I feel, make up only a small portion of possible errors. You should instead compare your quality score with several (20 or more) blocks of data for which a more conventional QA assessment has been made. You could perhaps regress quality score upon such factors as bias and precision at different concentrations, spike recoveries, blanks or results on CRM's such as UTS 1-4 or other Canmet reference materials. Without such a statistically valid demonstration, the application of quality score as a measure of data quality cannot be assumed to be meaningful.

3. With regard to the Methodology Section, too large a discrepancy exists between the first two choices of part A (15 vs 3 points). I believe this should be 5 vs 3 or 10 vs 6 points. Points subtracted from A should be added to D which is the more important factor and should be weighted higher.

I hope these comments will be useful.

Sincerely,

Peter Fowlie

Peter Fowlie
Laboratory Services Section.

cc: K. Conn

Canada

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Environment Canada Environnement Canada

Water Quality National Laboratory
Canada Centre for Inland Waters
867 Lakeshore Road, P.O. Box 5050,
Burlington, Ontario
L7R 4A6

Your file Votre reference

Our file Notre reference

December 5, 1984

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DEC 12 1984

Mr. D.R. Hart, Ph.D.
Applied Ecologist,
IEC Beak Consultants Ltd.,
6870 Goreway Drive
Mississauga, Ontario
L4V 1P1

Dear Mr. D.R. Hart;

I have your letter requesting my comments on the proposed criteria which you have developed for evaluation of data in the CANUT data base.

Following are the additions I feel should be included in your documents:

Criterion	Summary Part
Analytical Quality Control	Method Development and Validation. Laboratory Performance - Precision, Bias, confidence internals for the working concentration ranges (low, medium and high).
	Logical Checks and Standard Operating Procedure and General Laboratory Practices - use of within and between run duplicates.
	Use of Control Samples and Control Charts - for spiked recoveries and difference of within and between run paired valves.
	Interlaboratory Studies and Criteria for Rejection of certain outliers.

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Canada

Sampling Methodology

Sample Collection and Identification Prococols.

Field Analysis Records.

Criterion Representing Analytical Methodology

Component

A.) Sensitivity, Specificity, Precision and Scope of Method.

B.) Lab uses externally documented methods (i.e., subjected to critical peer review and published in open literature and validates methods).

Criterion Representing Analytical Quality Control

Component

E.) Routine use of replicates, standards and blank and use of SRMS developed by reliable organization; within and between run duplicates. (standard deviation and spikes plotted on the control chart.

Criterion Representing Sampling Methodology

Component
Sample Collection and Identification

A. Sample type (phase, matrix, etc.): adequate volume and/or weight for all analyses.

B. Location (position, depth, etc.): date/time of sampling. Name of person collecting sample. Date shipped.

D. Chain of sample custody (indiviual responsible, sample number, etc.): date/time of sampling. Name of person collecting sample. Date shipped and date when the sample was received in the laboratory.

N. Colour
O. Turbidity

Yours truly,

Afghan

Dr. B.K. Afghan
Chief, Water Quality National Laboratory

BKA/rt

APPENDIX 5

Error Rate Determinations for Verification of Criteria

TABLE A1: DETECTION LIMIT ERRORS FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY DETERMINATIONS IN ELLIOT LAKE, BANCROFT AND URANIUM CITY DATA

Element	Sample Type	No. of Samples	No.< DL Non-zero	Error Rate
Lead	Water	281	2	0.0070
	Vegetation	415	0	0
	Solids	247	3	0.0120
	All	953	5	0.0050
Nickel	Water	230	0	0
	Vegetation	243	2	0.0080
	Solids	170	1	0.0060
	All	643	3	0.0050
Copper	Water	230	0	0
	Vegetation	243	0	0
	Solids	168	0	0
		641	0	0
Cobalt	Water	224	0	0
	Vegetation	190	2	0.0110
	Solids	161	1	0.0060
	All	575	3	0.0050

TABLE A2: OUTLIERS FROM RADIUM-226, BARIUM AND CALCIUM DISTRIBUTIONS IN ELLIOT LAKE, BANCROFT AND URANIUM CITY TAILINGS

Distribution	Control Area	Elliot Lake	Bancroft Area	Uranium City	Average
Radium-226					
No. Out	1	1	0	0	2
N	27	74	43	54	198
Error Rate	0.0370	0.0135	0	0	0.0101
Barium (NAA)					
No. Out	1	2	1	1	5
N	47	116	68	75	306
Error Rate	0.0213	0.0170	0.0150	0.0130	0.0163
Calcium (NAA)					
No. Out	1	1	1	0	3
N	53	95	73	75	296
Error Rate	0.0189	0.0110	0.0137	0	0.0101

TABLE A3: OUTLIERS FROM RADIUM-226-LEAD-210 AND CALCIUM-MAGNESIUM RELATIONSHIPS IN ELLIOT LAKE, BANCROFT AND URANIUM CITY

Relationship	Control Area	Elliot Lake	Bancroft Area	Uranium City	Average
Water					
Ra-226 - Pb-210					
No. Out	1	1	0	0	2
N	48	63	46	53	210
Error Rate	0.0208	0.0159	0	0	0.0095
Water					
Ca - Mg					
No. Out	0	-	0	1	1
N	21	-	21	52	94
Error Rate	0	-	0	0.0192	0.0106
Vegetation					
Ra-226 - Pb-210					
No. Out	0	1	2	2	5
N	102	156	87	48	393
Error Rate	0	0.0064	0.0230	0.0417	0.0127

TABLE A3: OUTLIERS FROM RADIUM-226-LEAD-210 AND CALCIUM-MAGNESIUM RELATIONSHIPS IN ELLIOT LAKE, BANCROFT AND URANIUM CITY (CONT'D)

Relationship	Control Area	Elliot Lake	Bancroft Area	Uranium City	Average
Vegetation					
Ca - Mg					
No. Out	0	1	1	0	2
N	63	108	61	47	279
Error Rate	0	0.0093	0.0164	0	0.0072
Tailings/Soil					
Ra-226 - Pb-210					
No. Out	0	1	1	1	3
N	34	81	45	55	215
Error Rate	0	0.0123	0.0222	0.0182	0.0140
Tailings/Soil					
Ca - Mg					
No. Out	-	1	-	0	1
N	-	93	-	59	152
Error Rate	-	0.0108	-	0	0.0066

FIGURE AI.1 1980-82 N=634

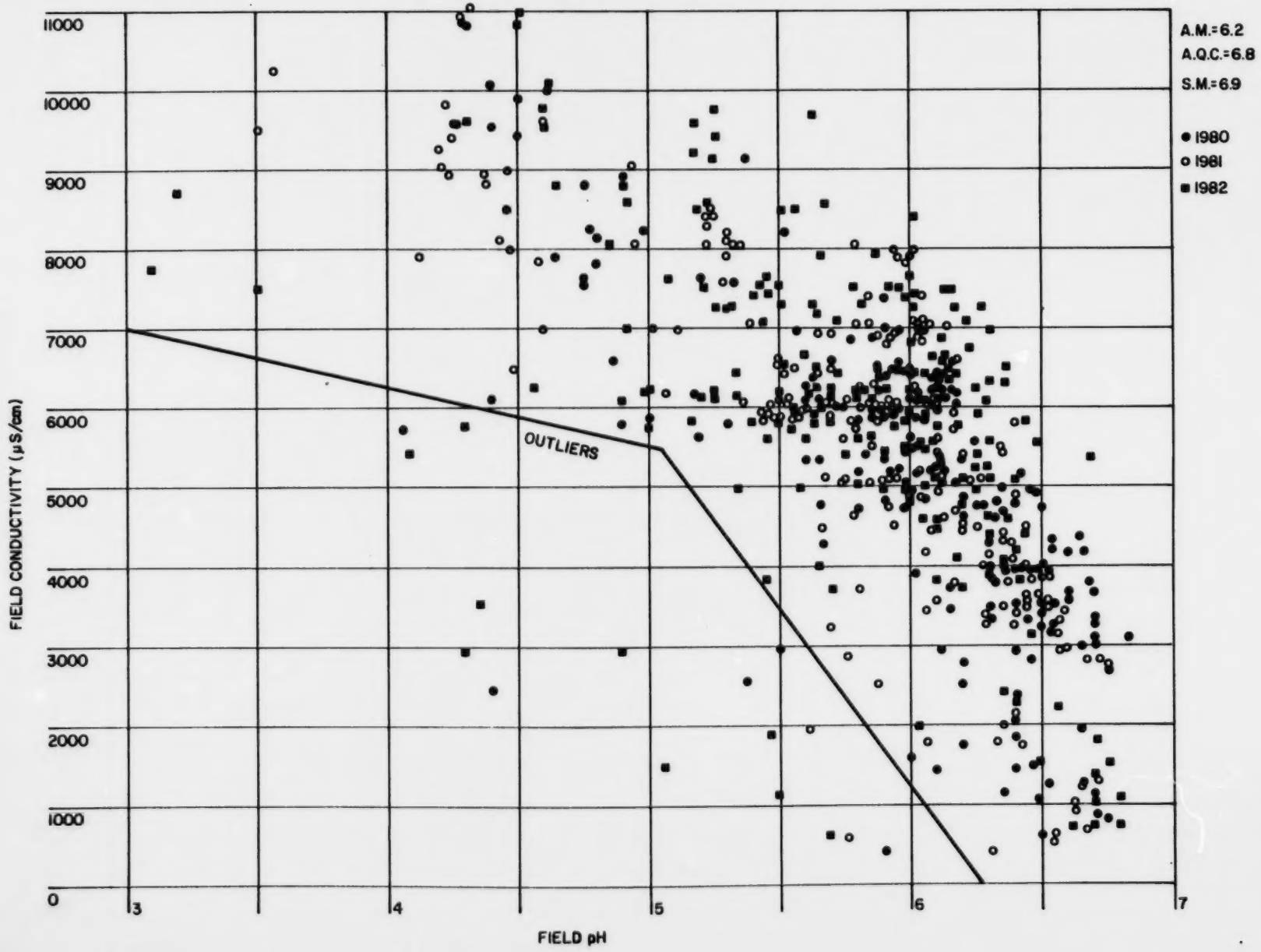


FIGURE A1.2 1983 DATA N=92

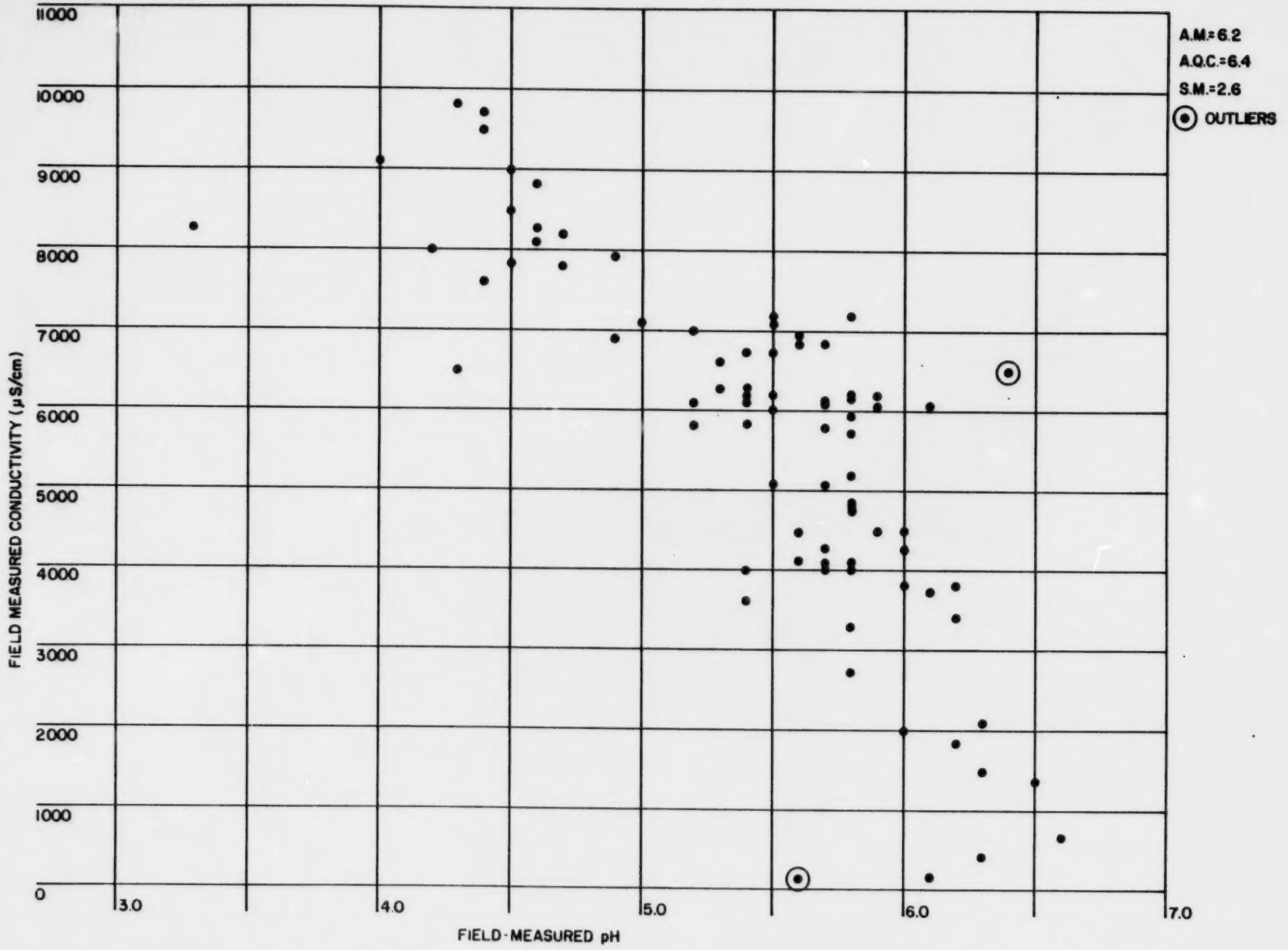


FIGURE A1.3 1984 DATA N=139

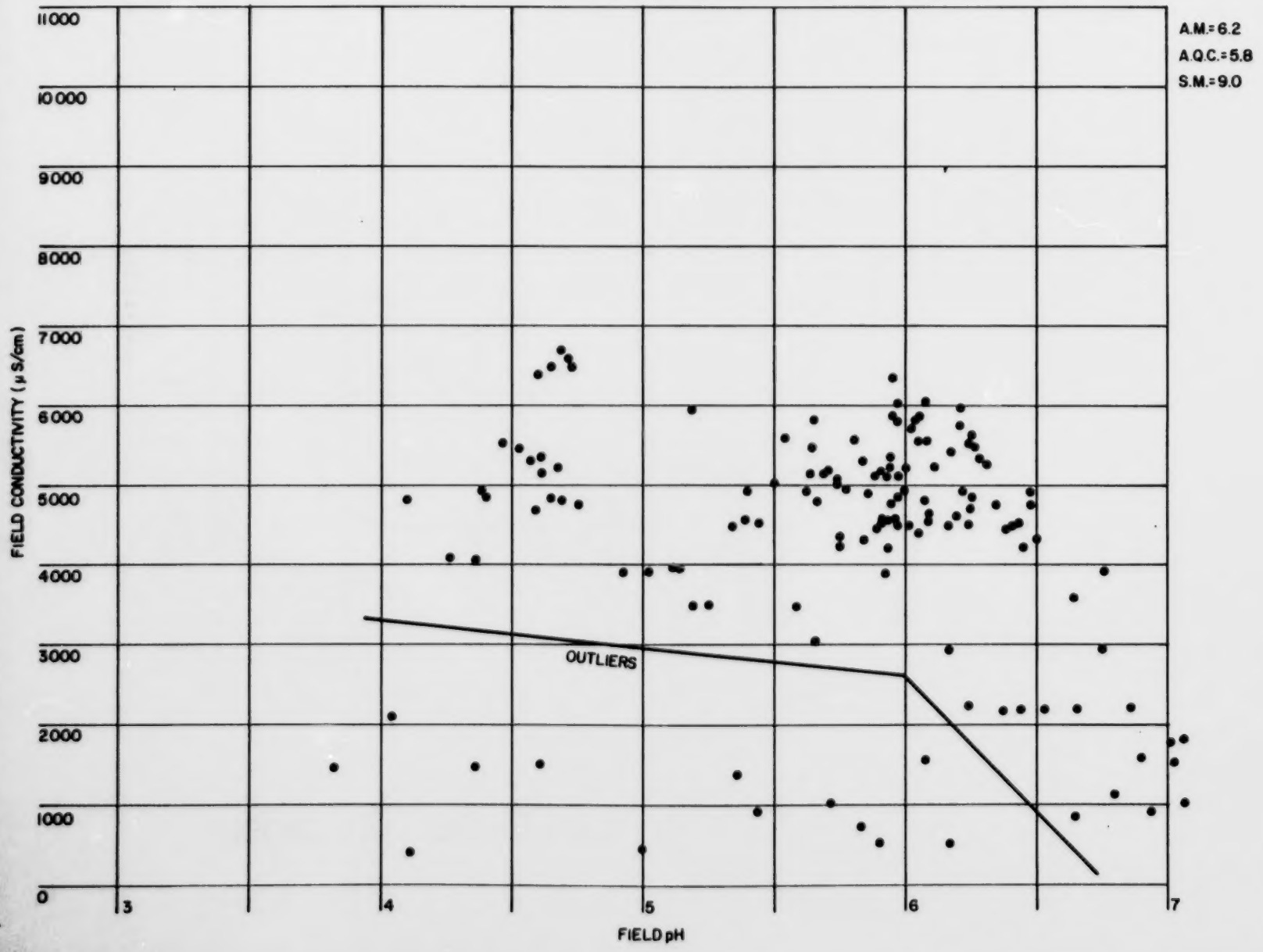


FIGURE A2.1 1980-81 DATA N=81

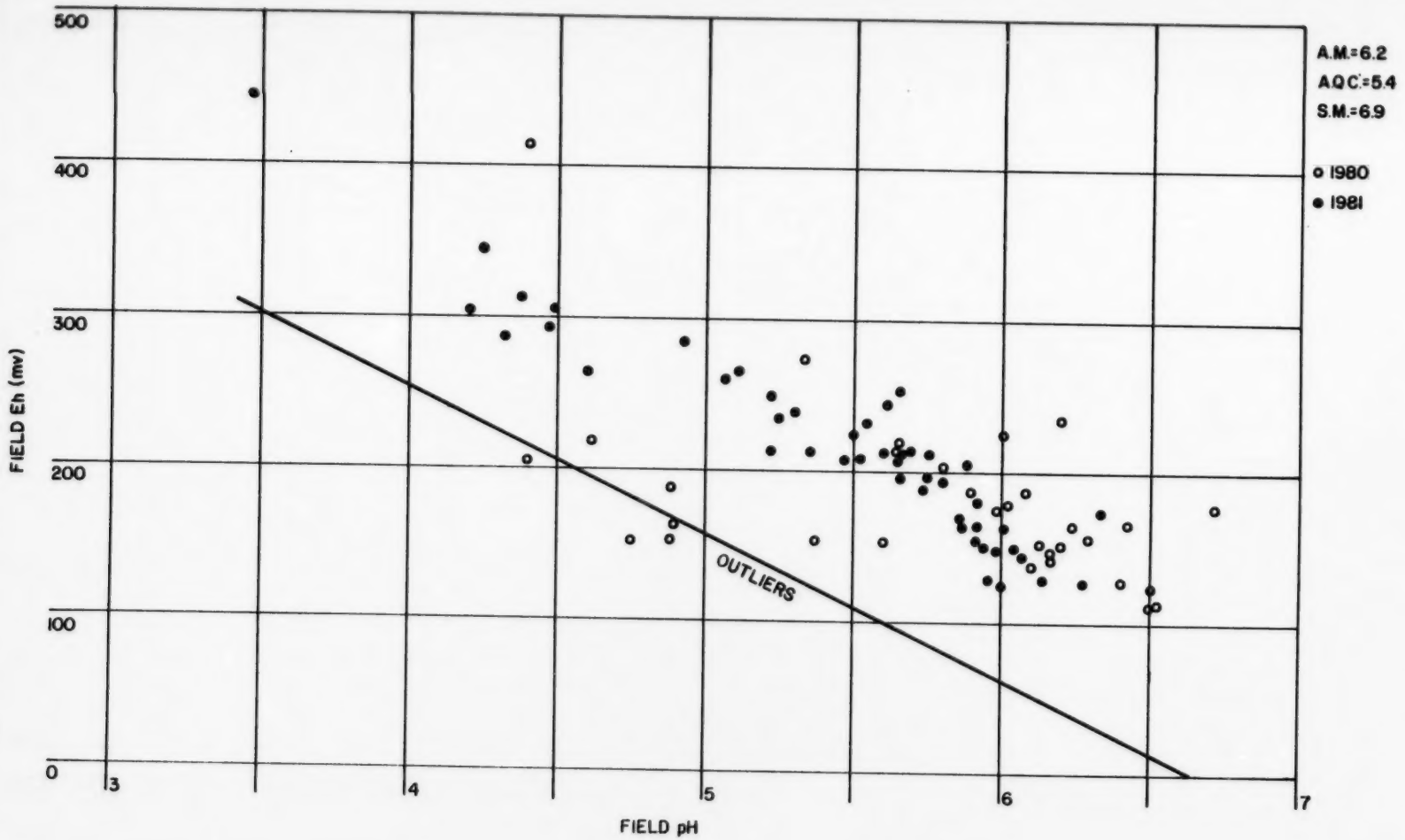


FIGURE A2.2 1983 DATA N=92

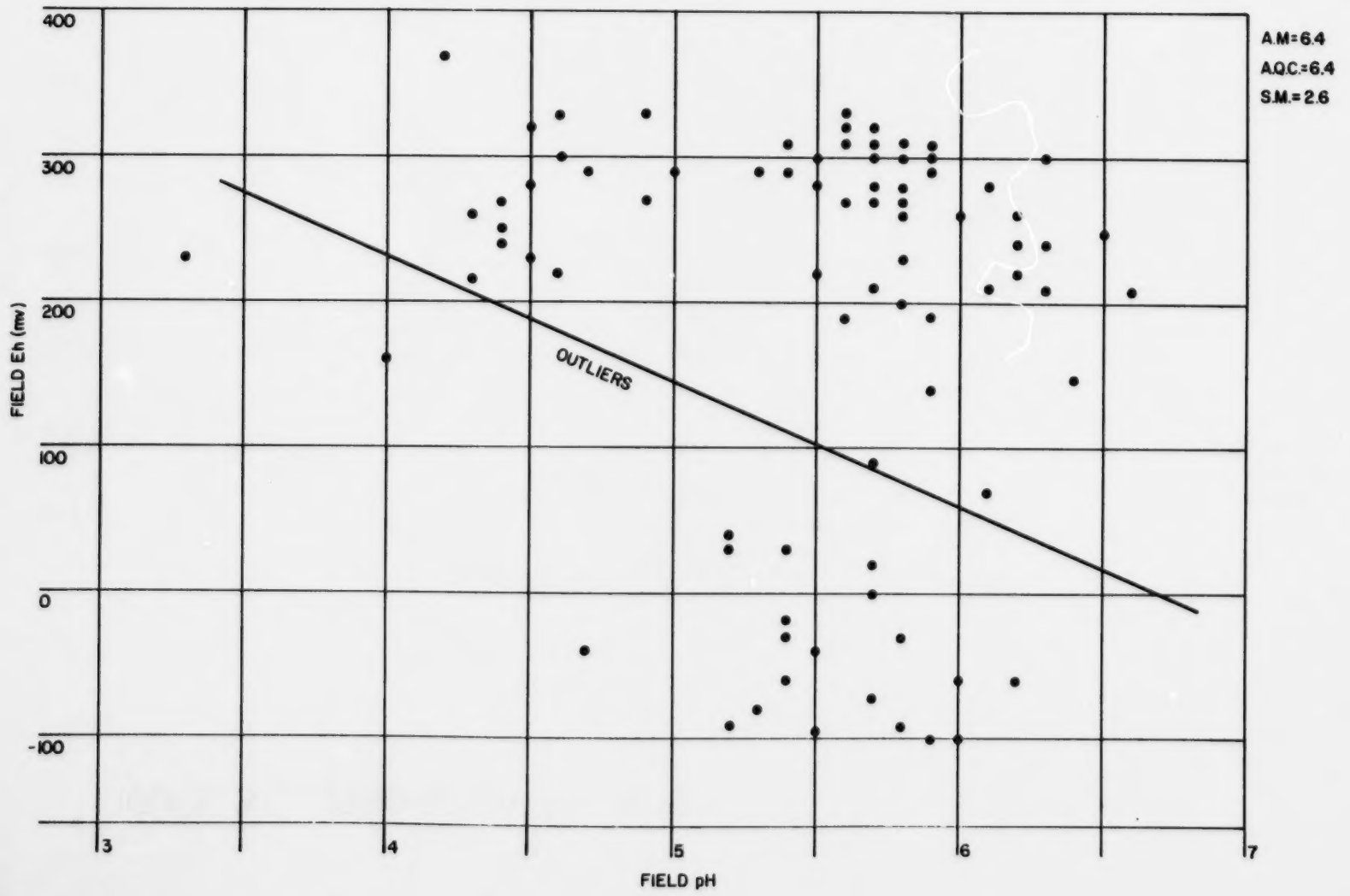


FIGURE 3.1 1980-82 DATA N=194

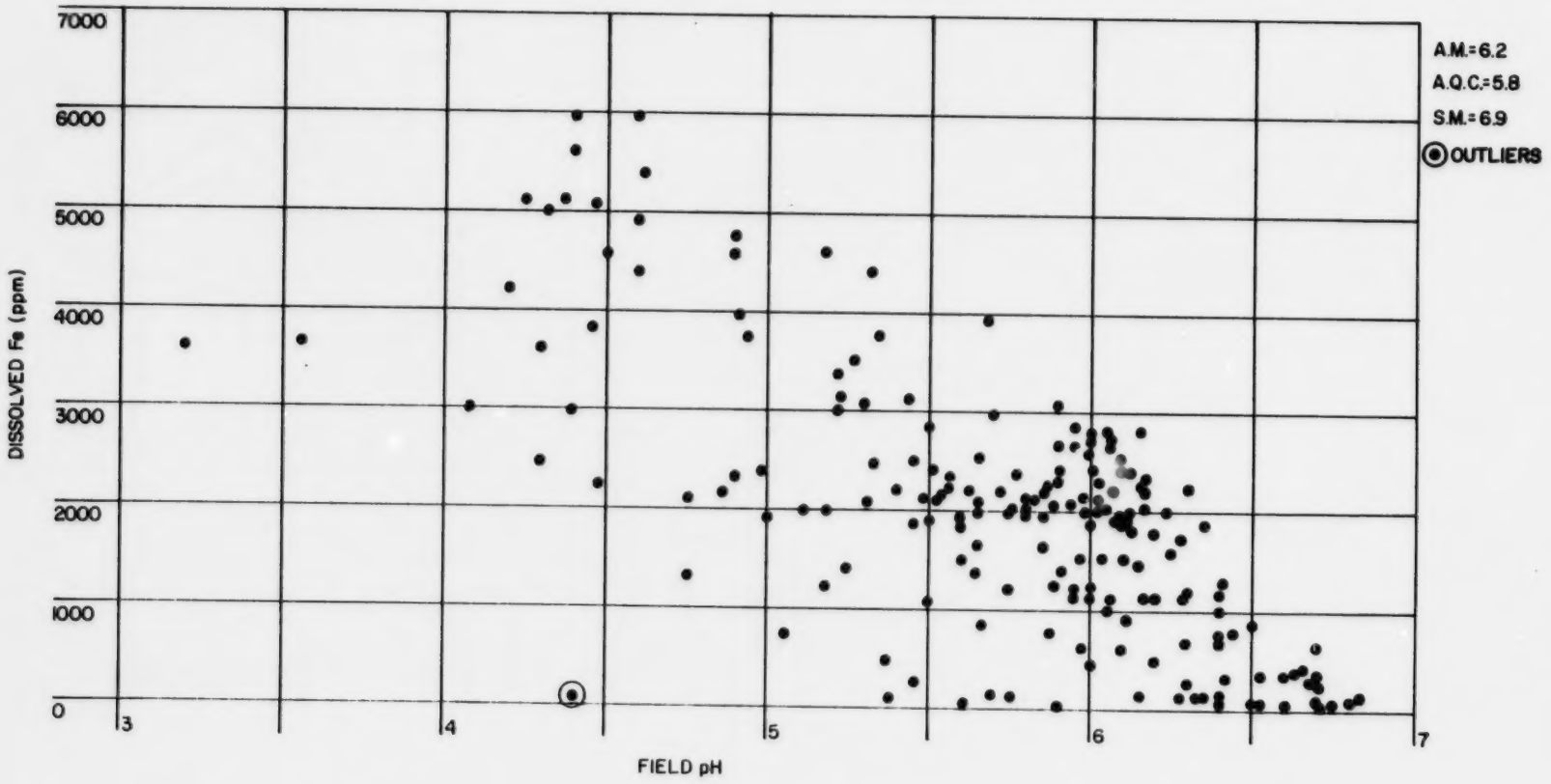


FIGURE A3.2 1983 DATA N=92

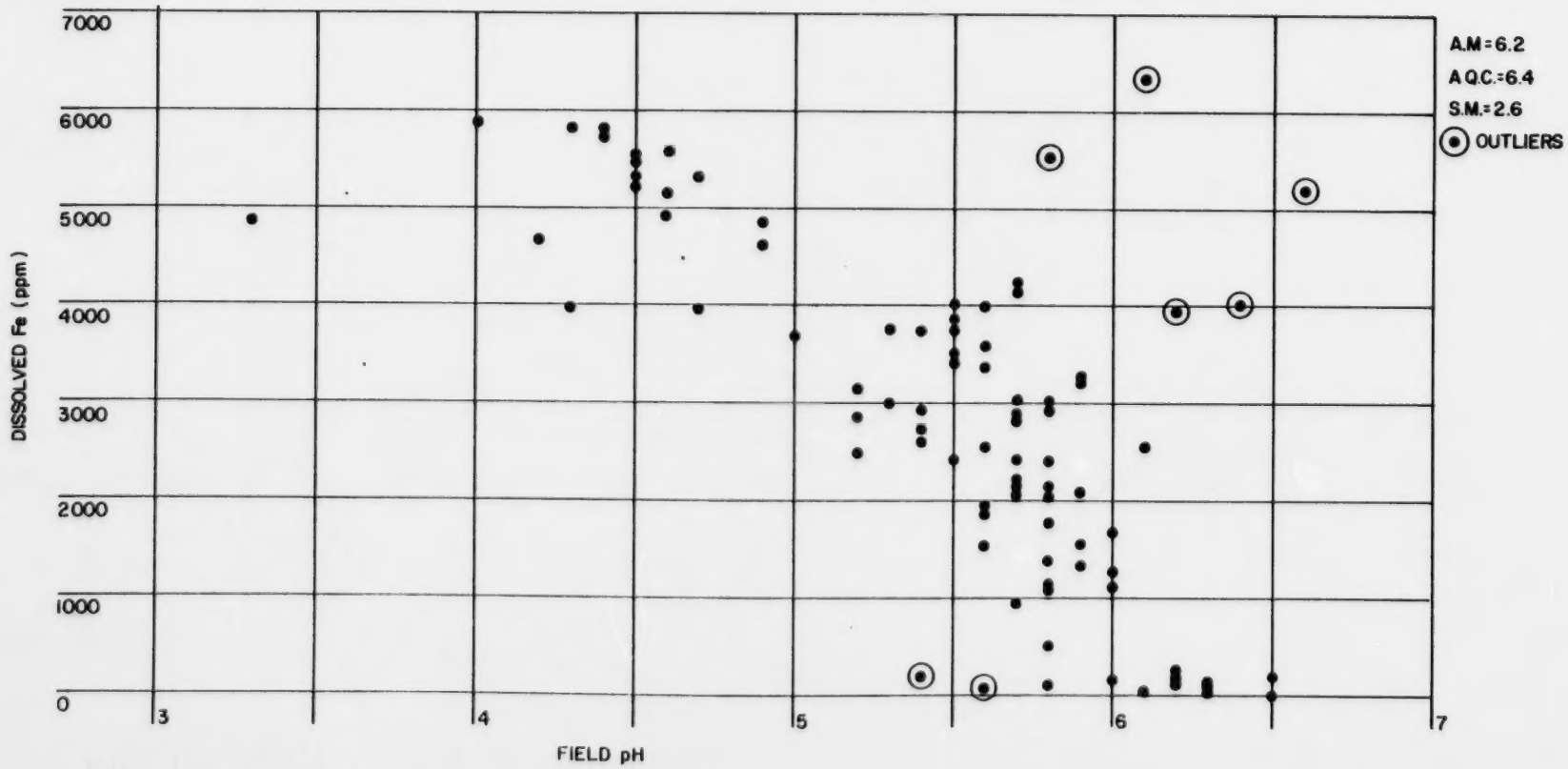


FIGURE A3.3 1984 DATA N=100

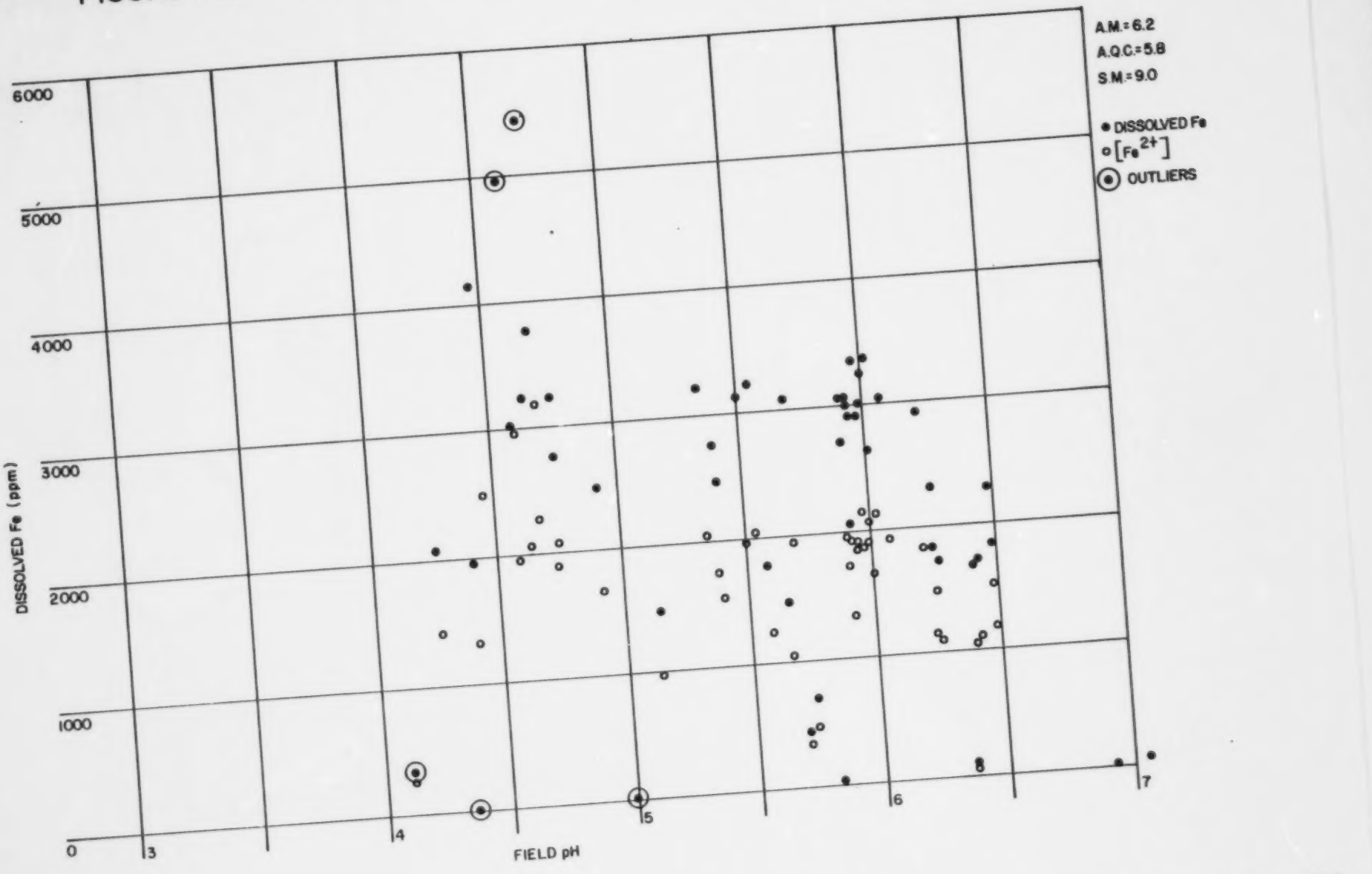


FIGURE A4.1 1982 DATA N=194

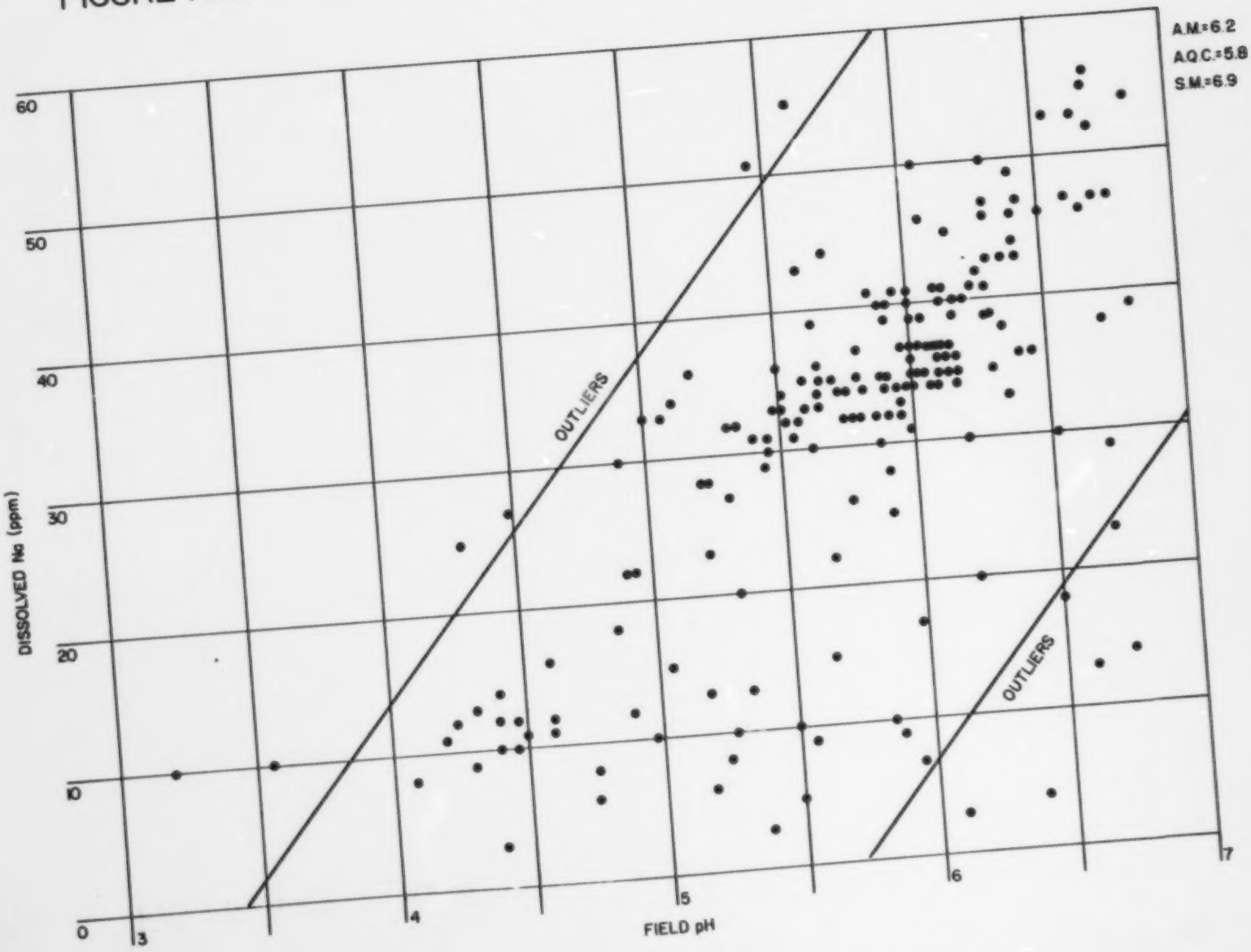


FIGURE A4.2 1984 DATA N=50

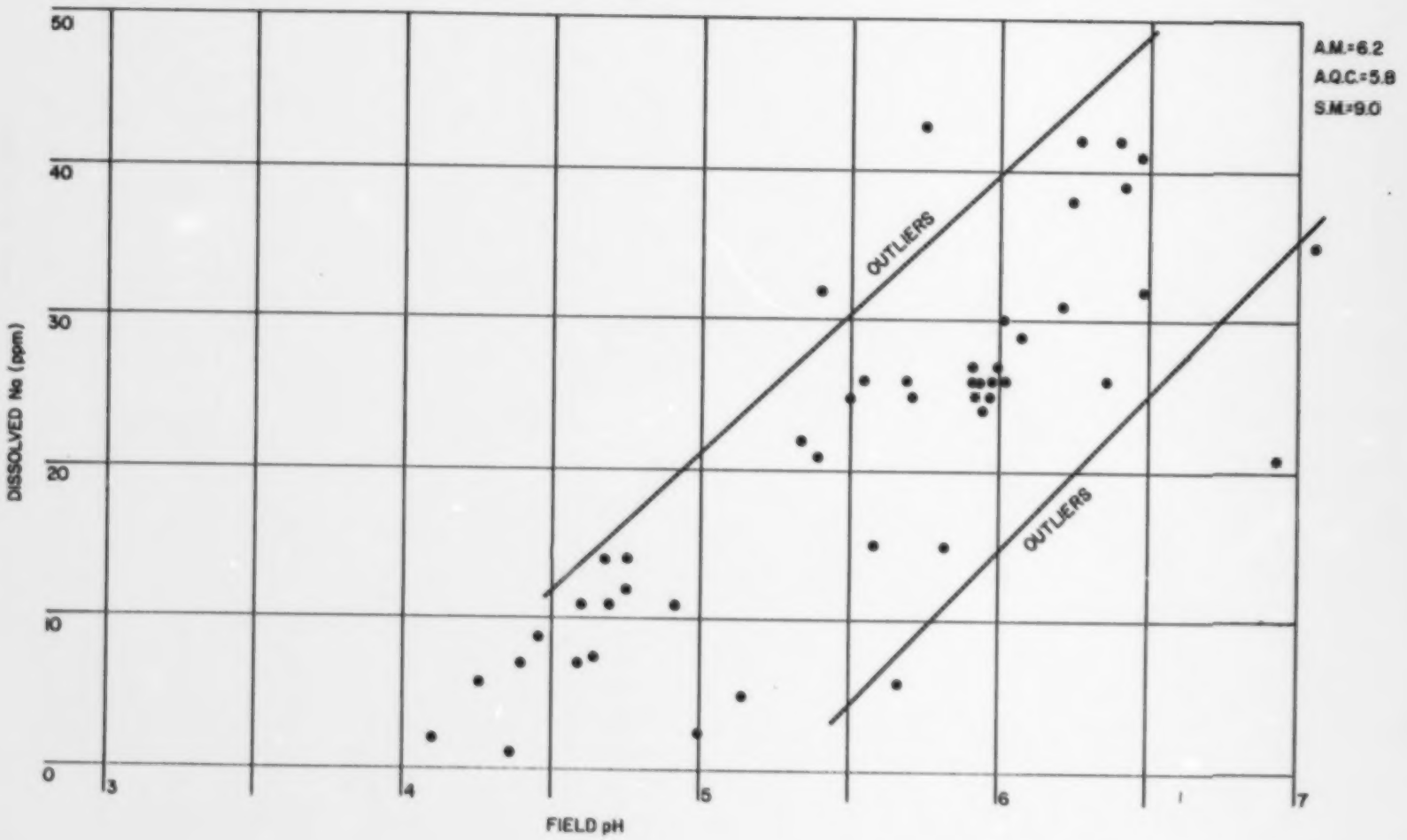


FIGURE A5.1 1980-82 DATA N=194

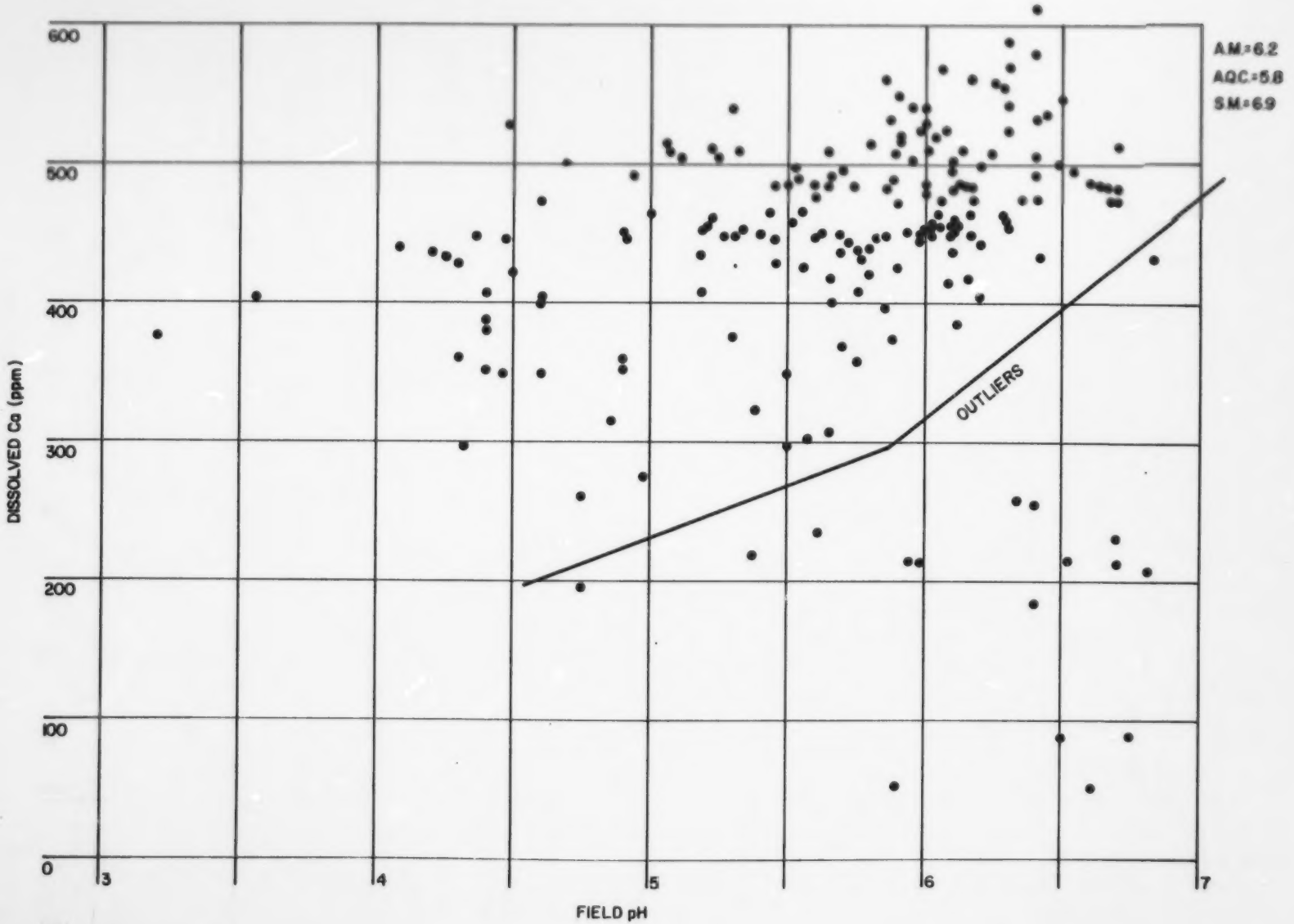


FIGURE A5.2 1984 DATA N=50

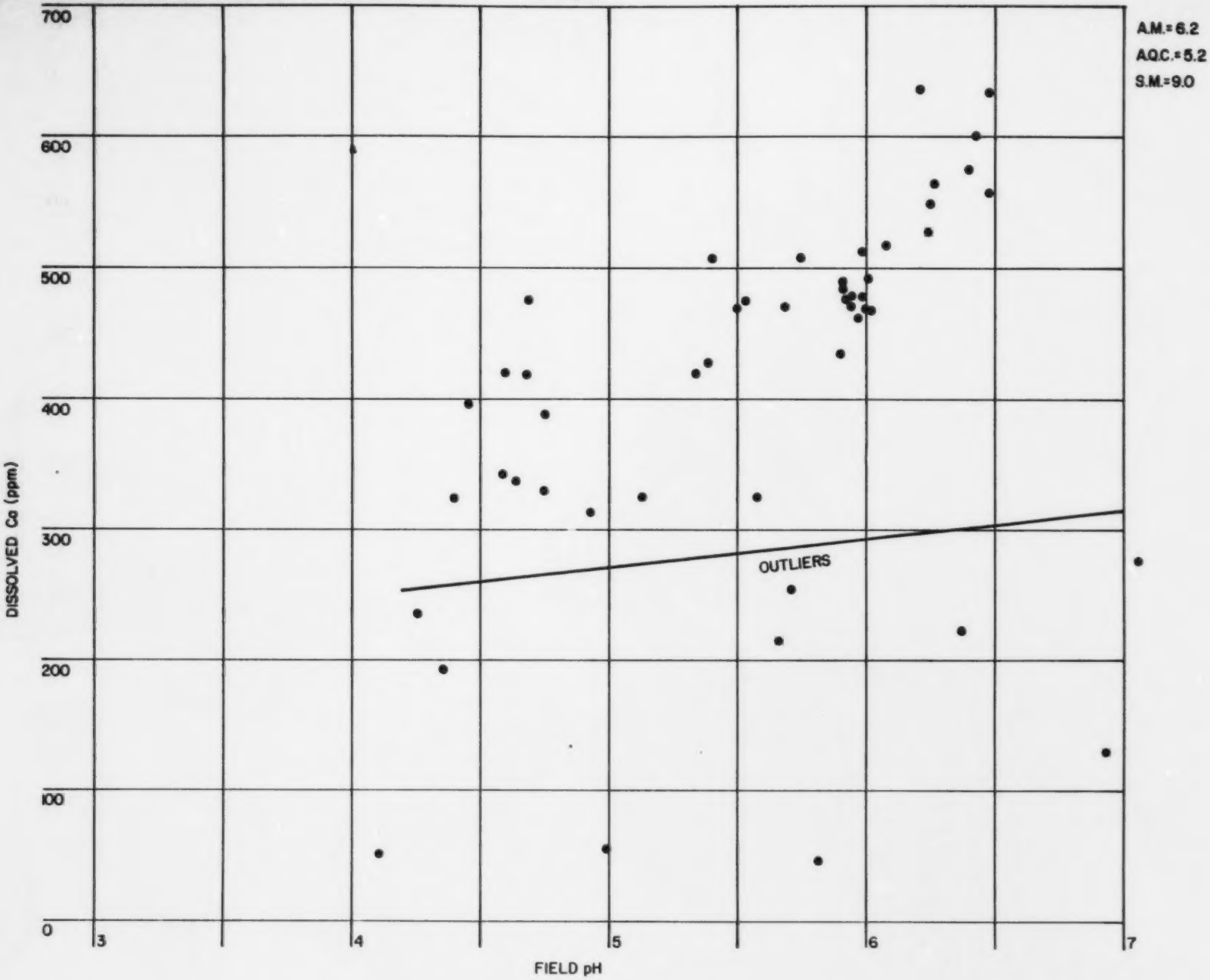
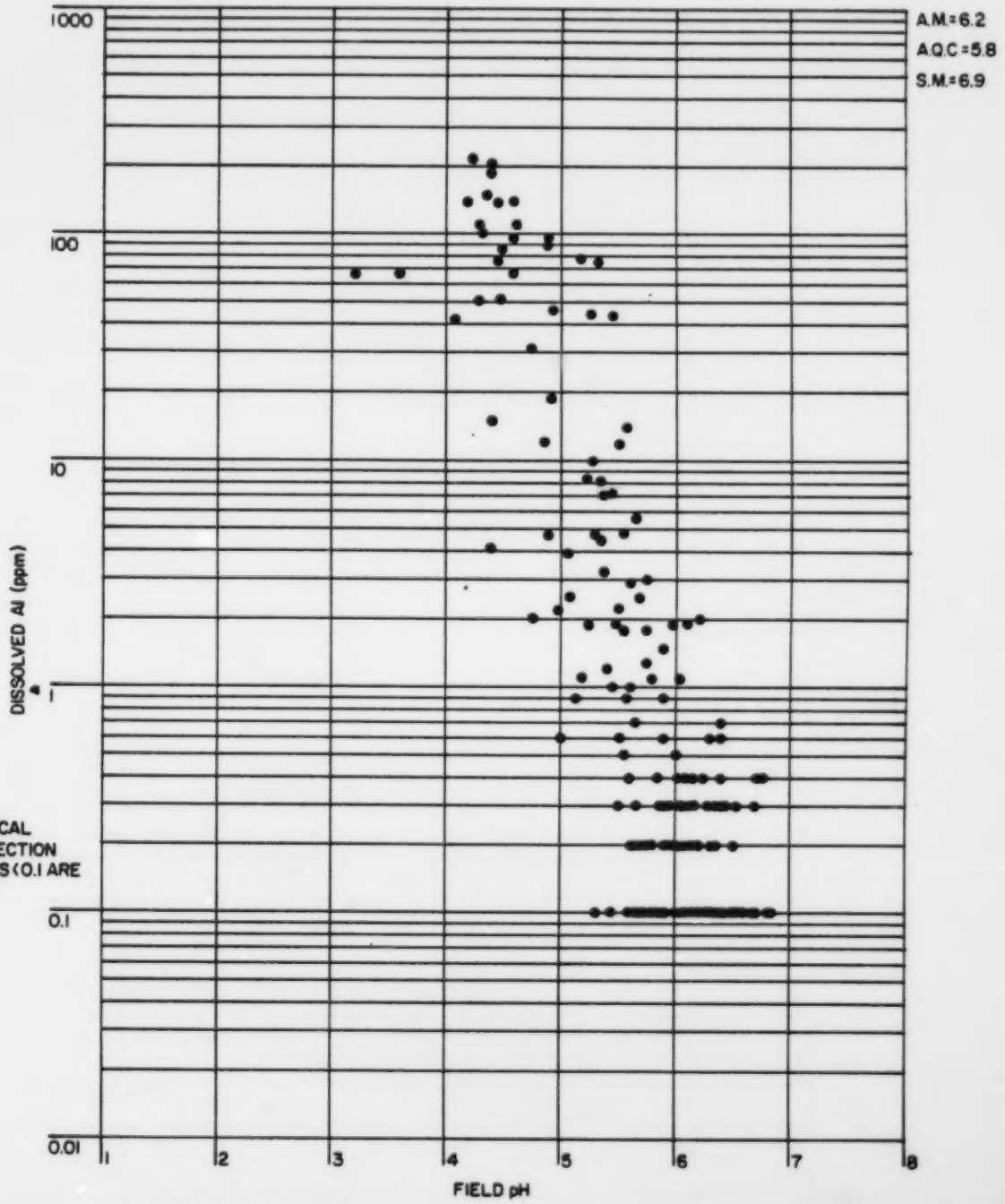


FIGURE A6.1 1980-82 DATA N=194



1980-82 ANALYTICAL ANALYTICAL DETECTION LIMIT (ALL VALUES <0.1 ARE REPORTED AS 0.1

VALUES RECORDED AS o ARE BELOW THE VARIABLE DETECTION LIMIT (0.2 OR 0.3) OF 1981

FIGURE A6.2 1983 DATA N=84

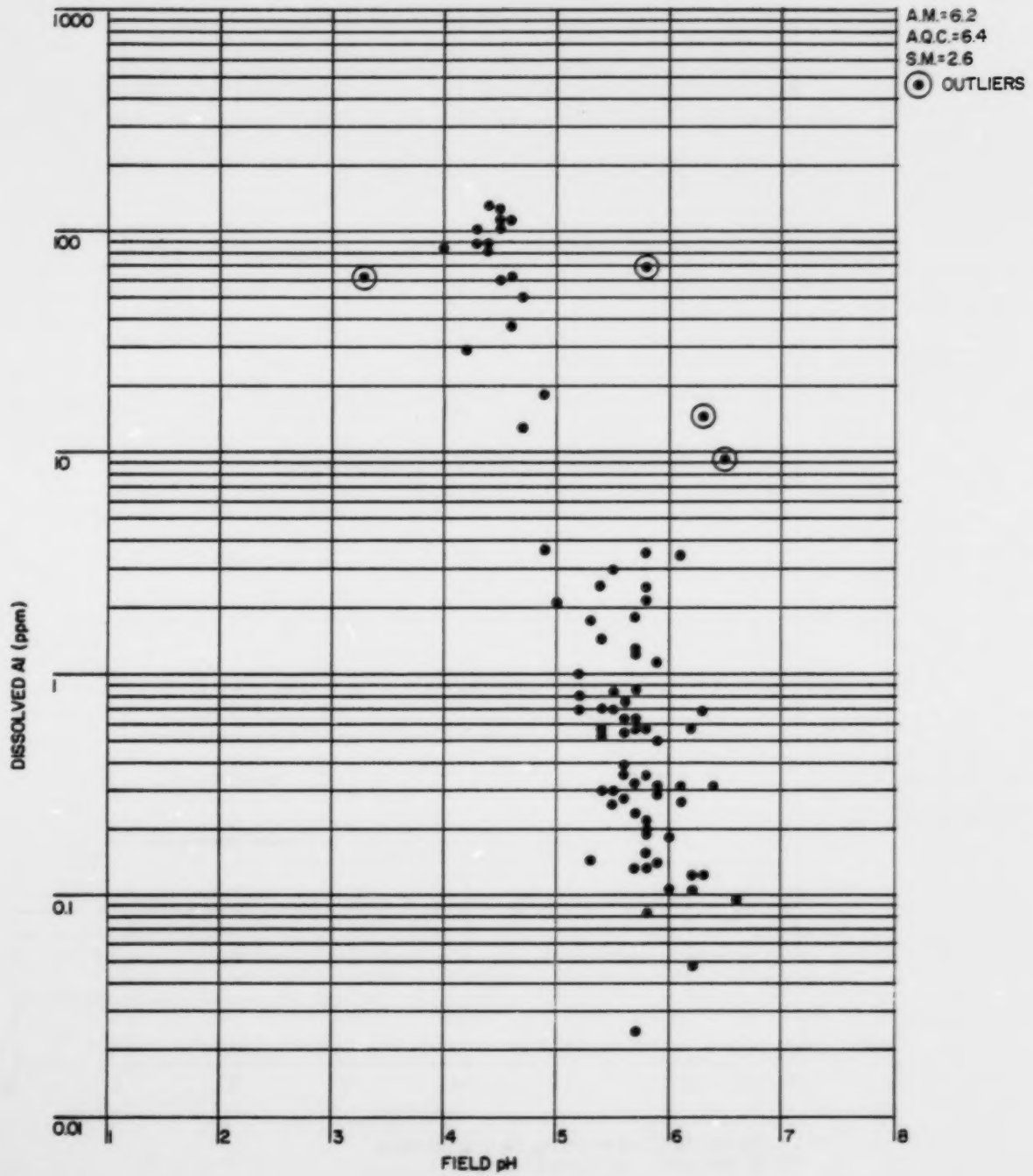


FIGURE A6.3 1984 DATA N=73

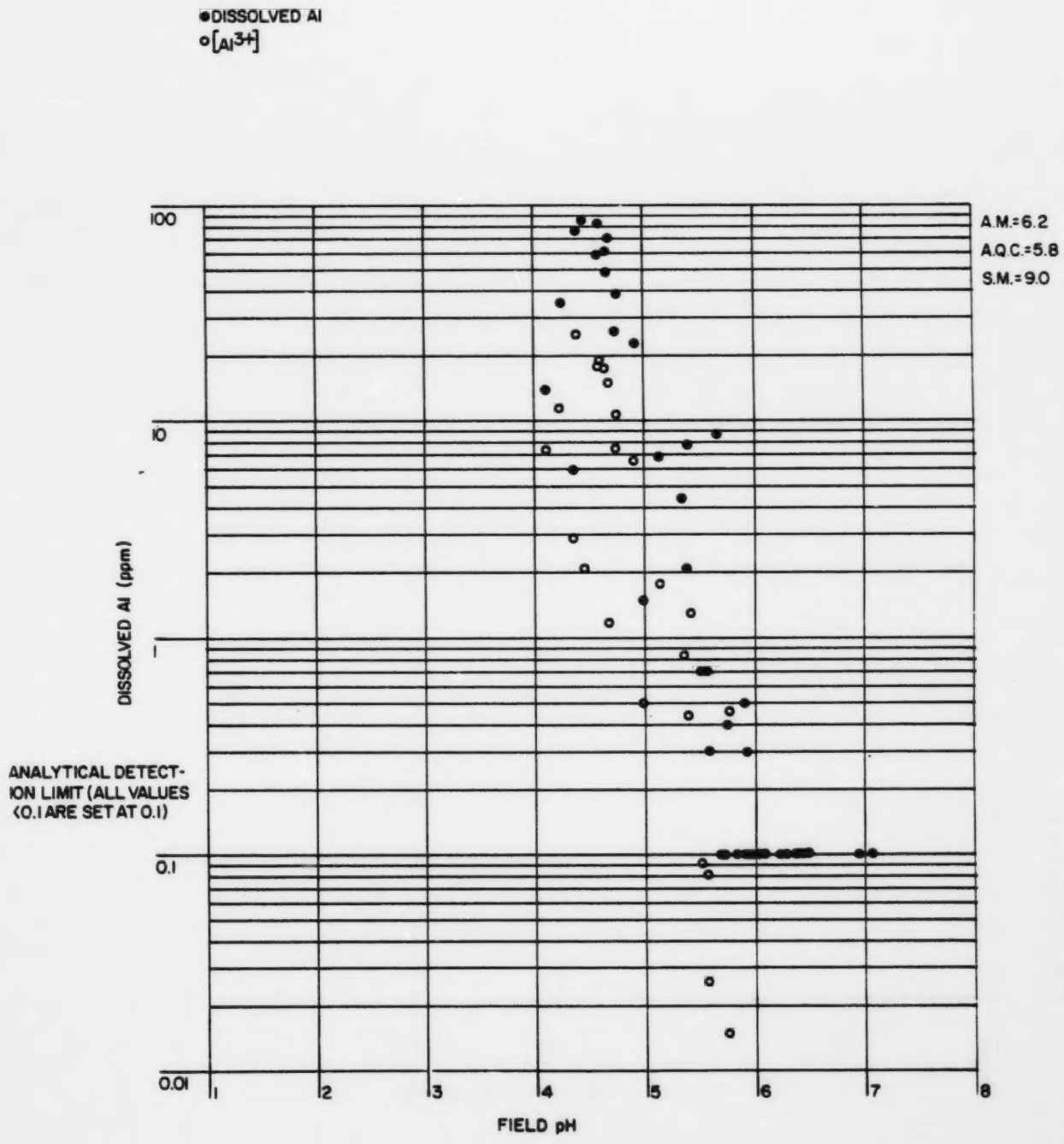


FIGURE A 7.1 1982 DATA N=59

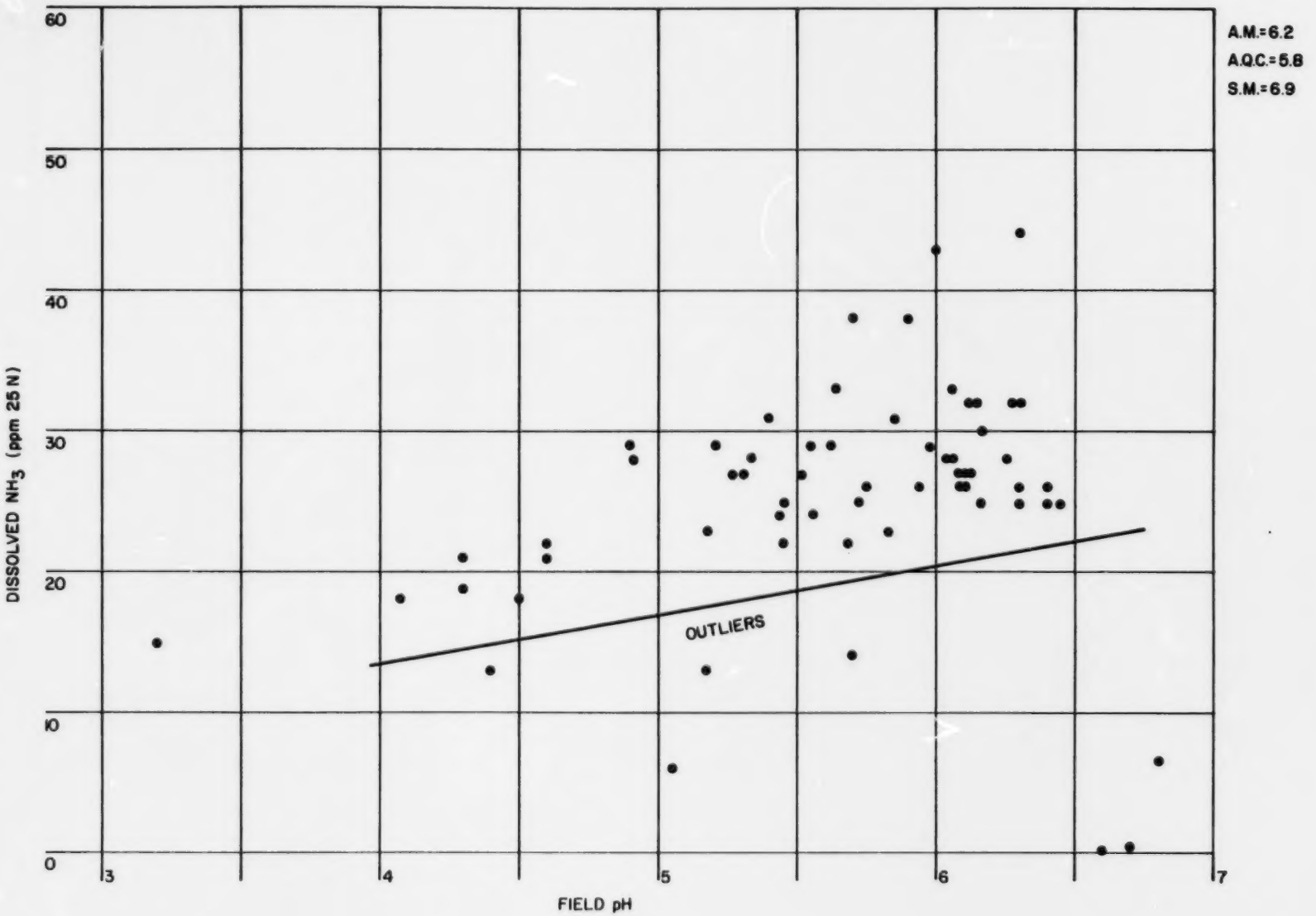


FIGURE A7.2 1984 DATA N=50

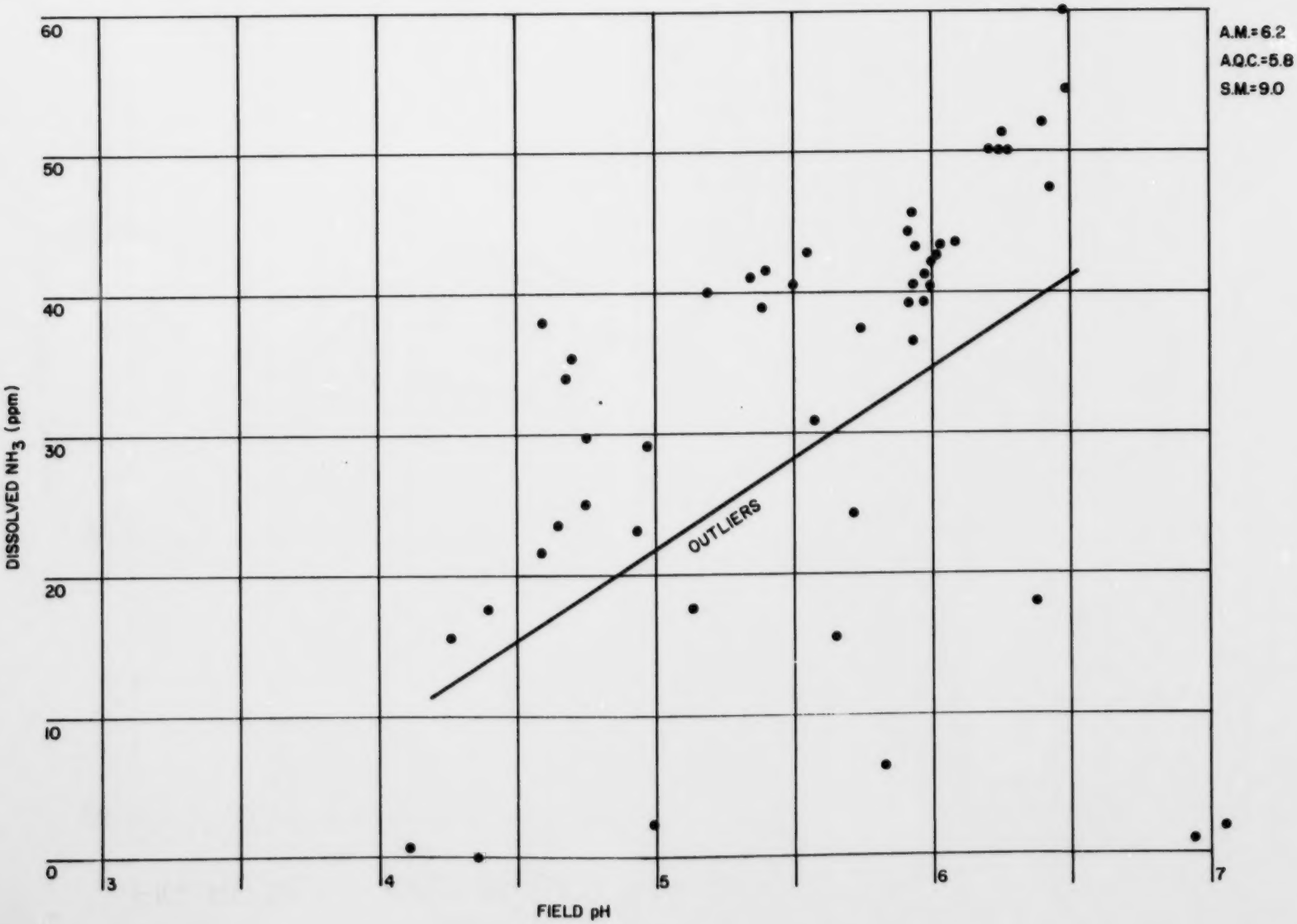


FIGURE A8.1 1980-82 DATA N=194

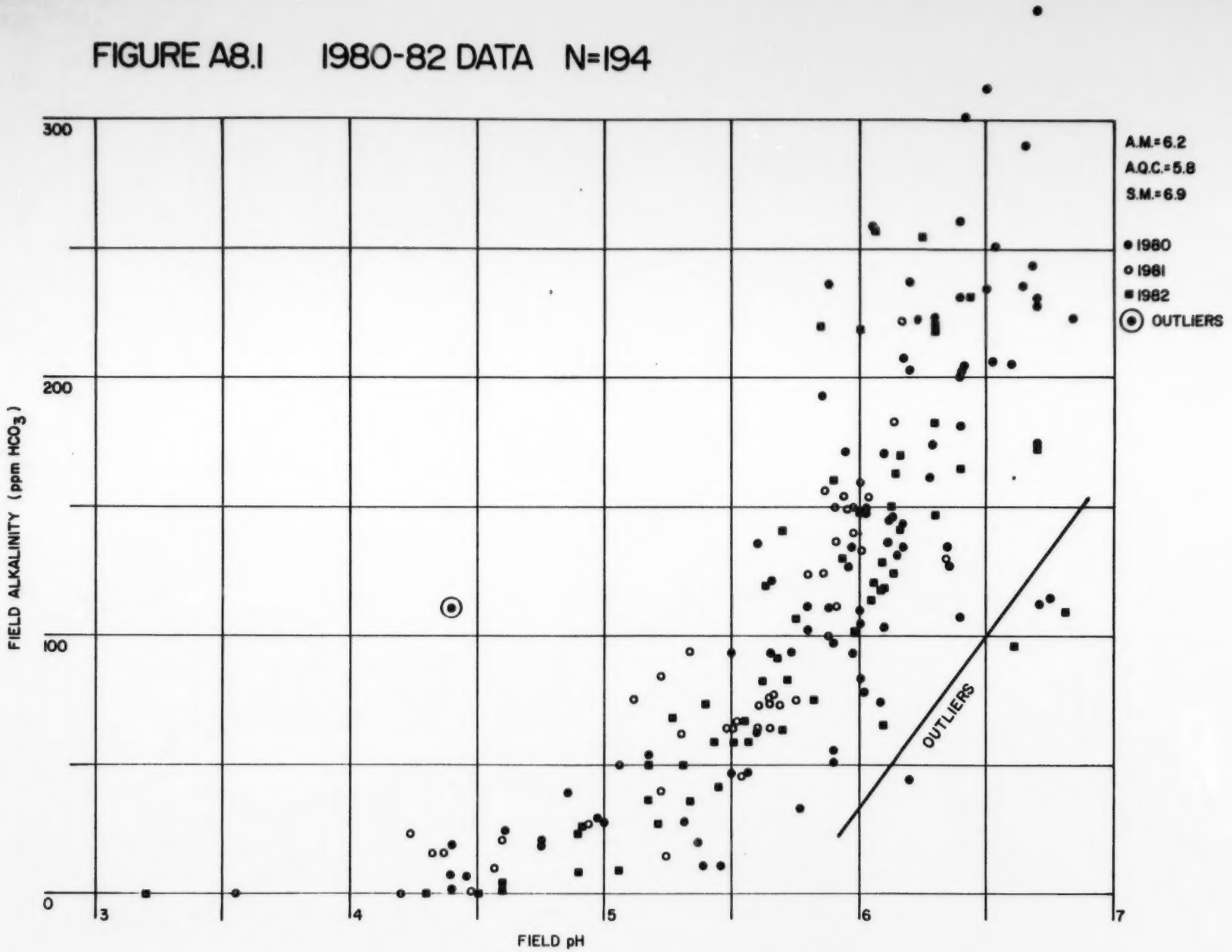


FIGURE A8.2 1984 DATA N=49

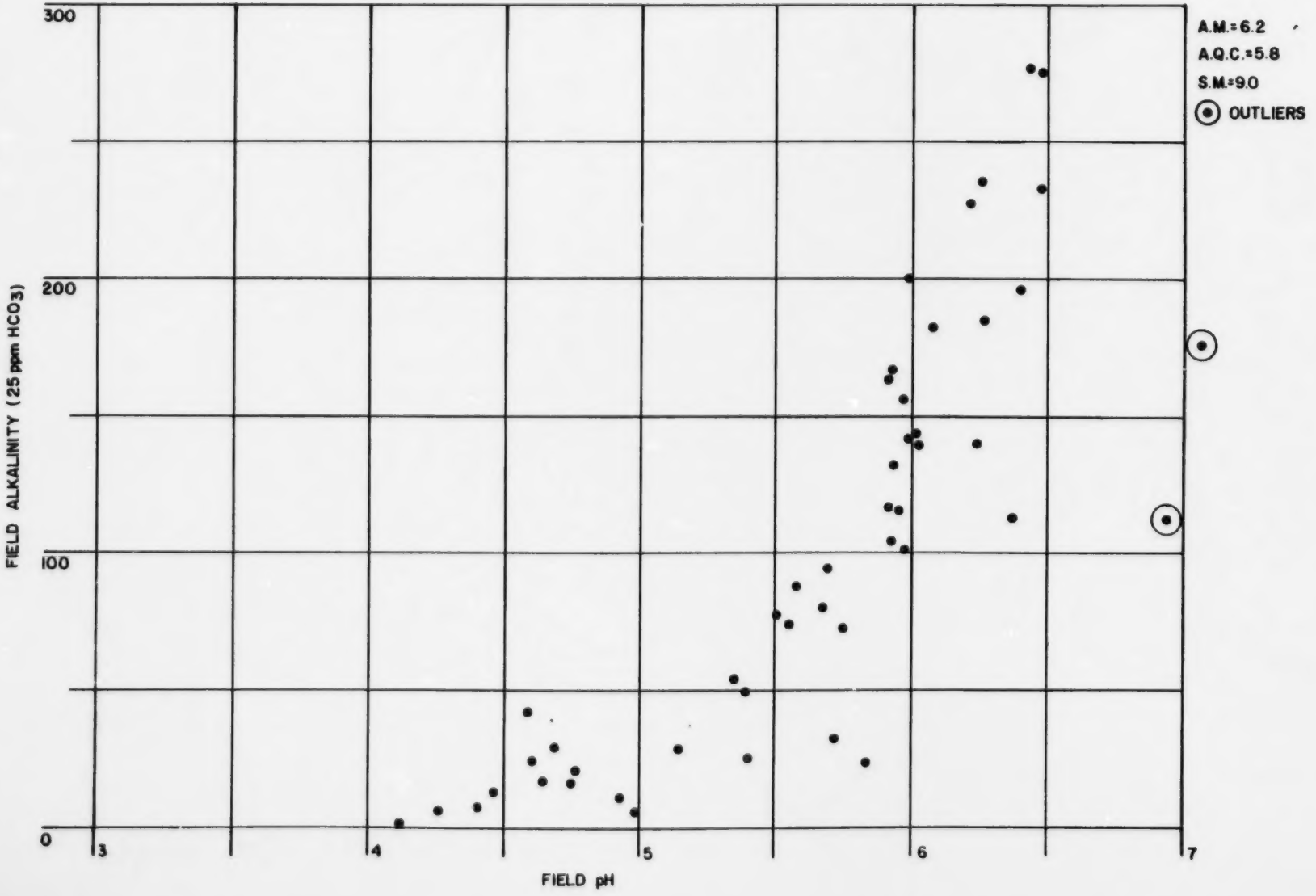
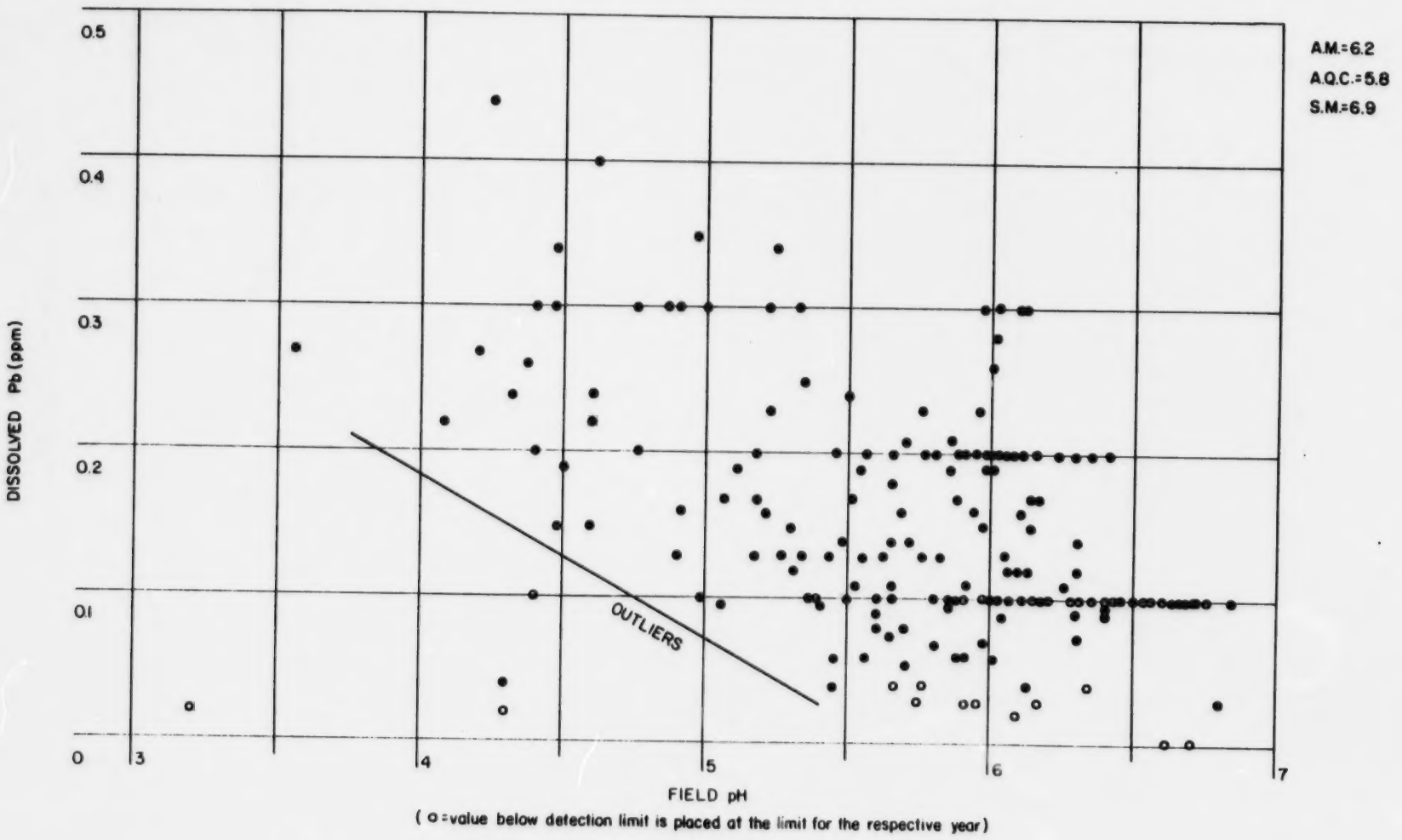


FIGURE A9.1 1980-1982 DATA N=194



(o=value below detection limit is placed at the limit for the respective year)

FIGURE A9.2 1984 DATA N=50

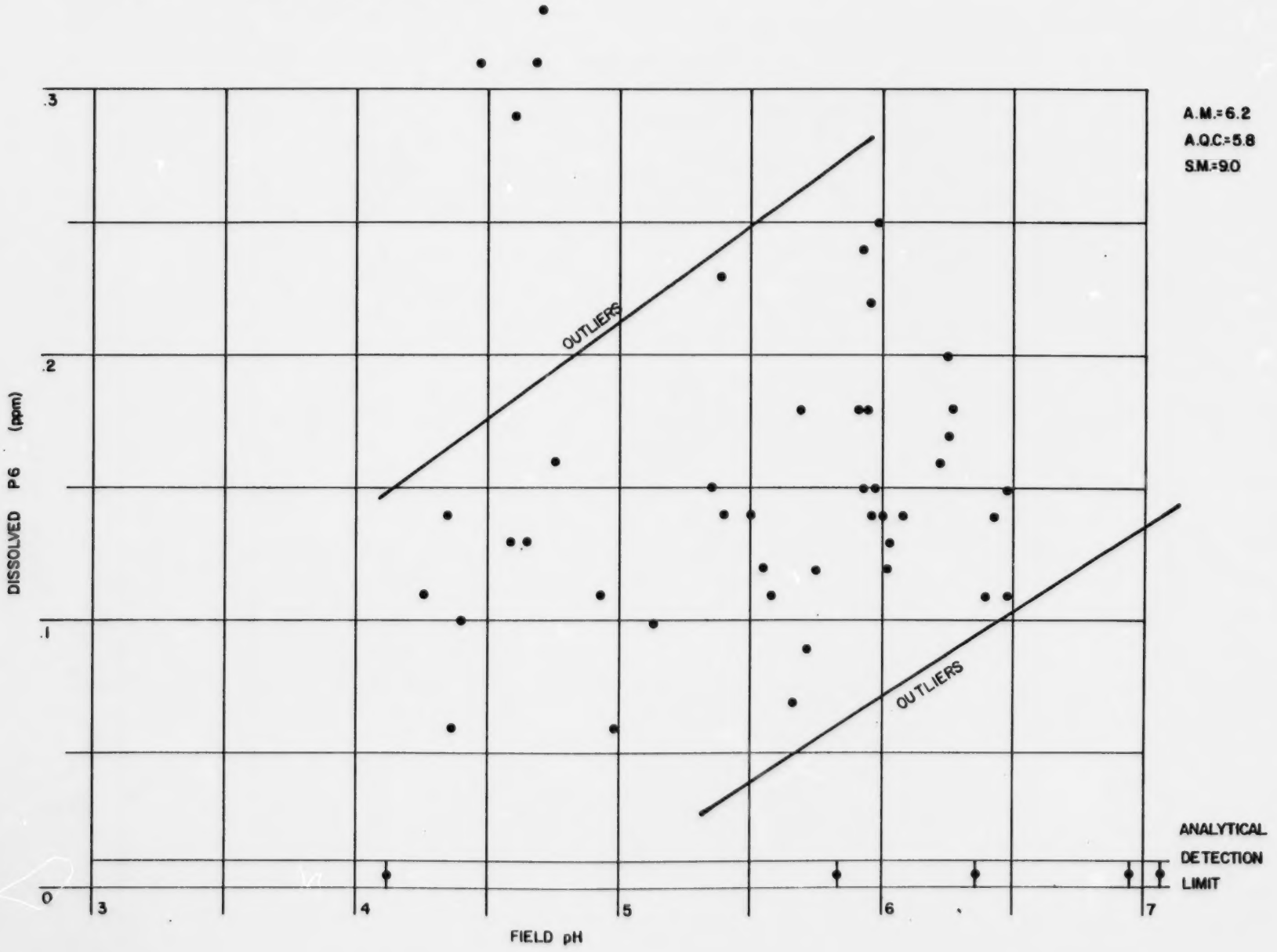


FIGURE A10.1 1980-82 DATA N=194

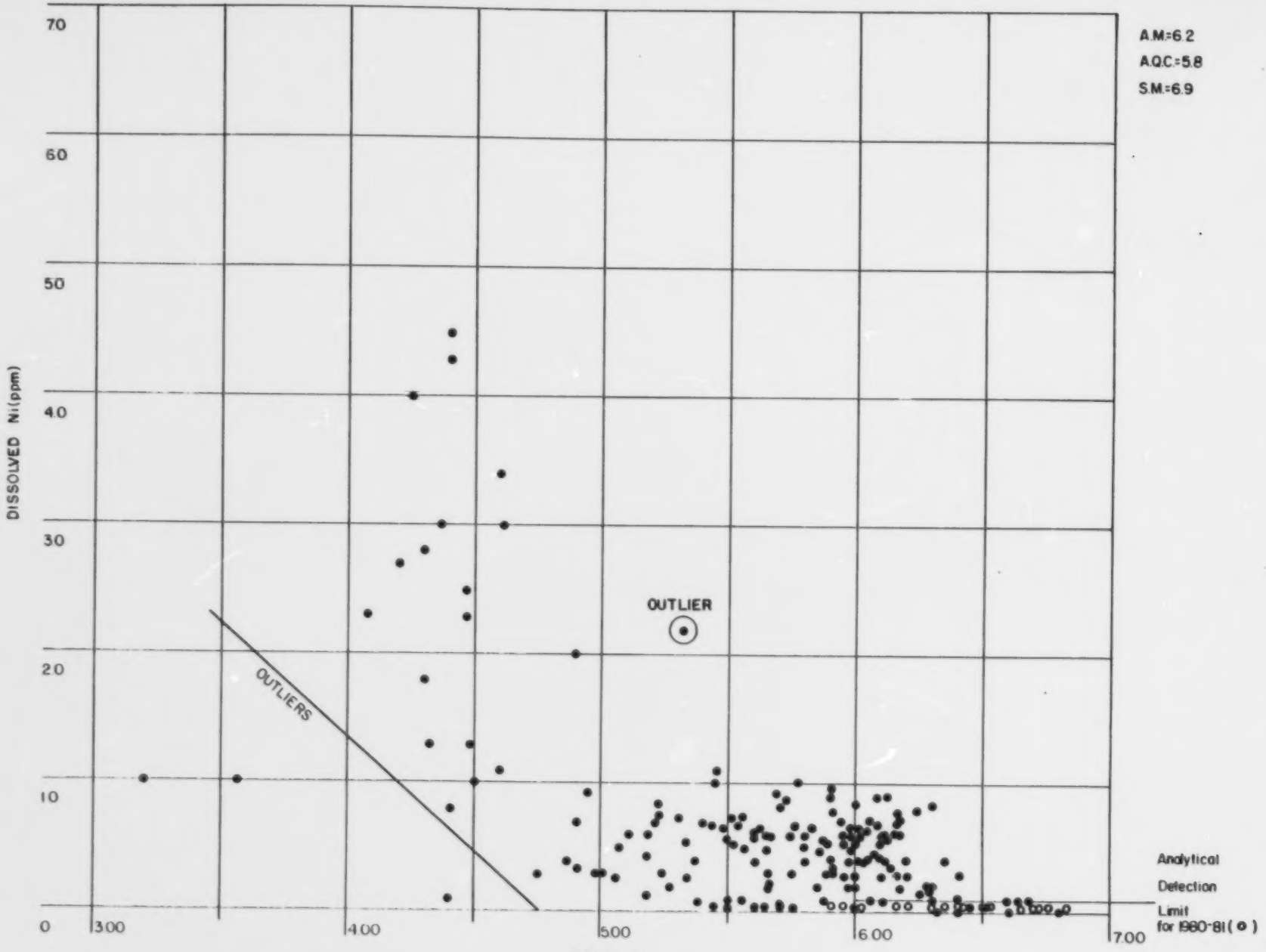


FIGURE A10.2 1984 DATA N=98

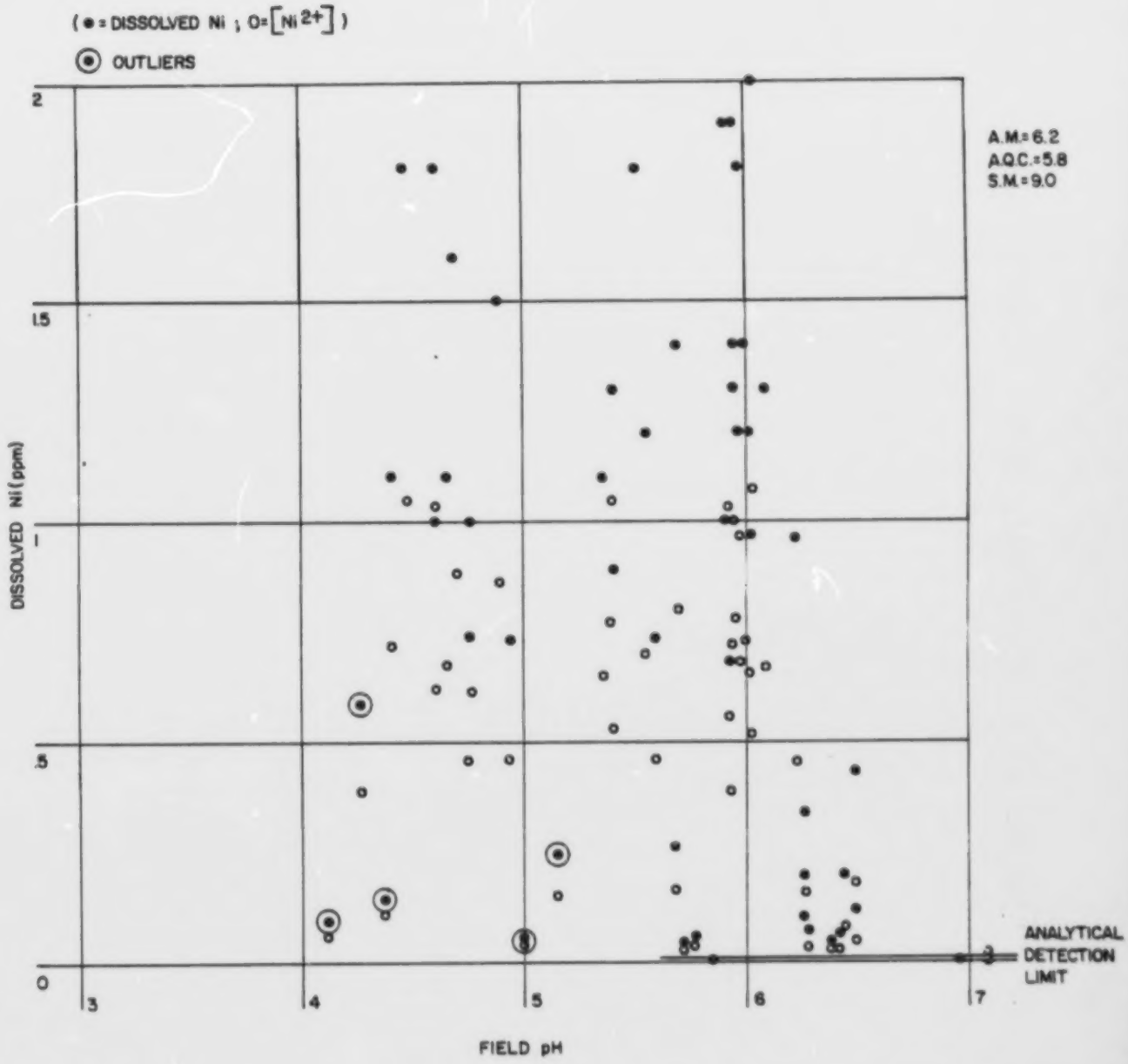


FIGURE A11.1 1980-1982 DATA CANMET ANALYSES N=55

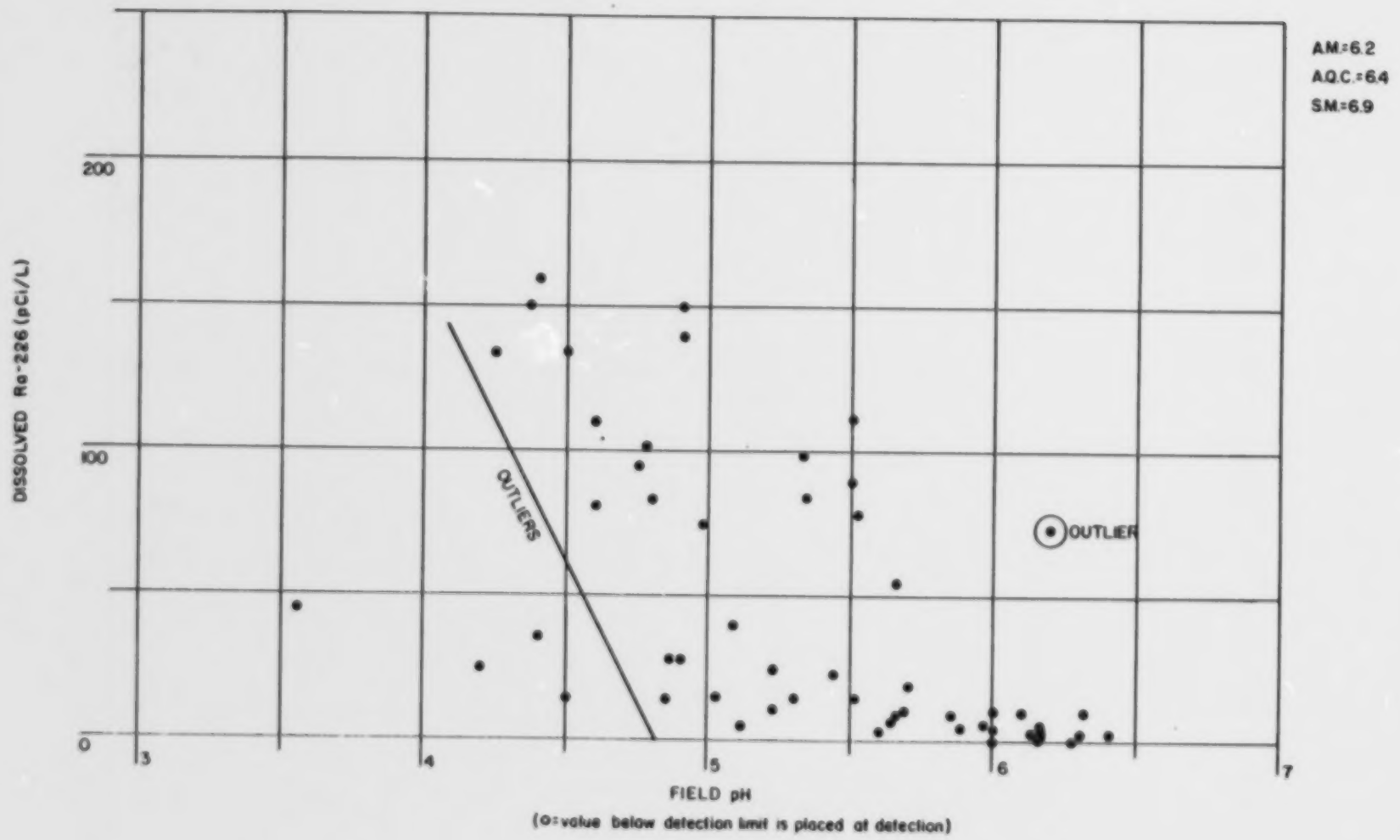


FIGURE A11.2 1983 DATA N=92

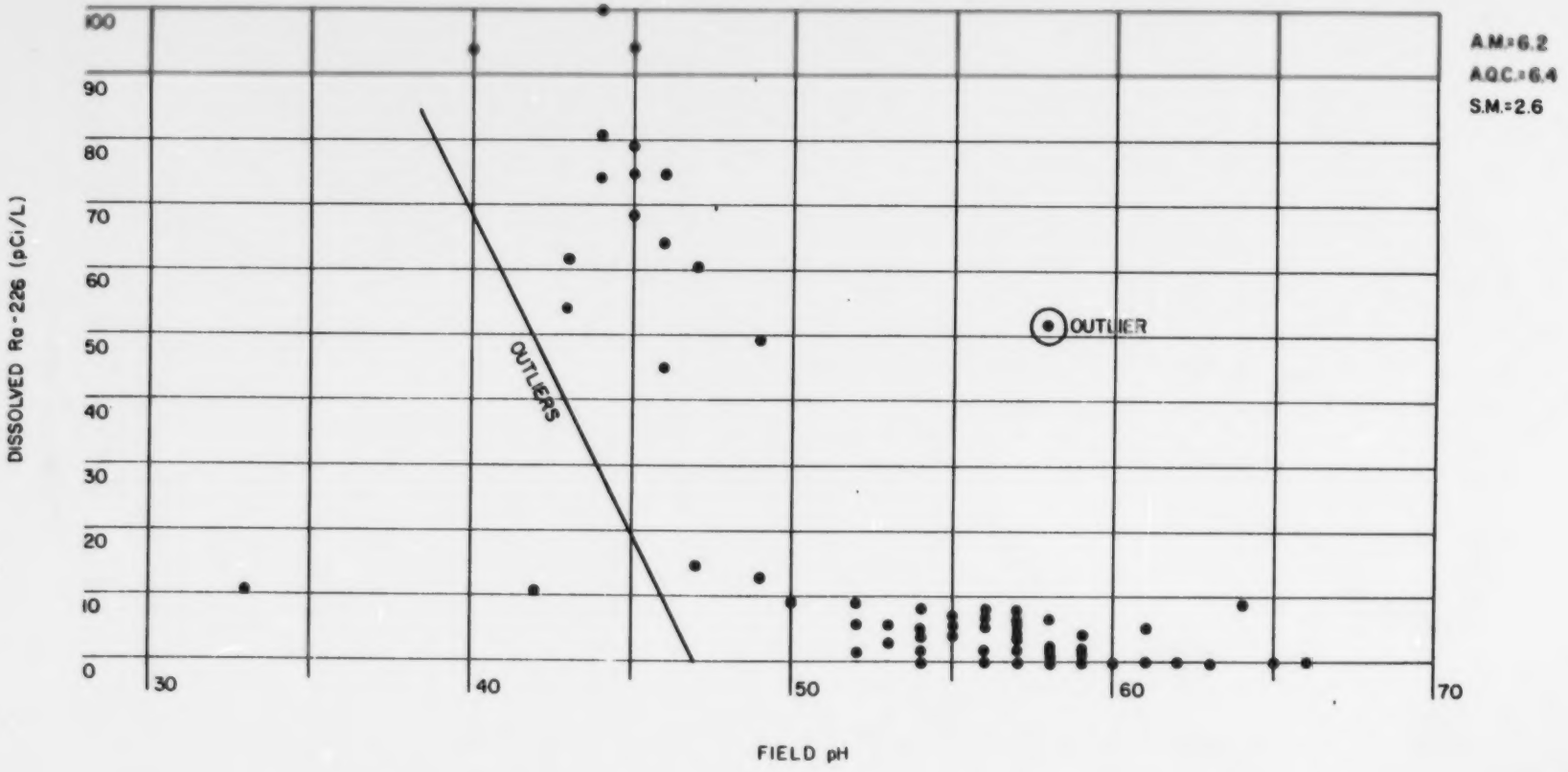


FIGURE A11.3 1984 DATA N=50

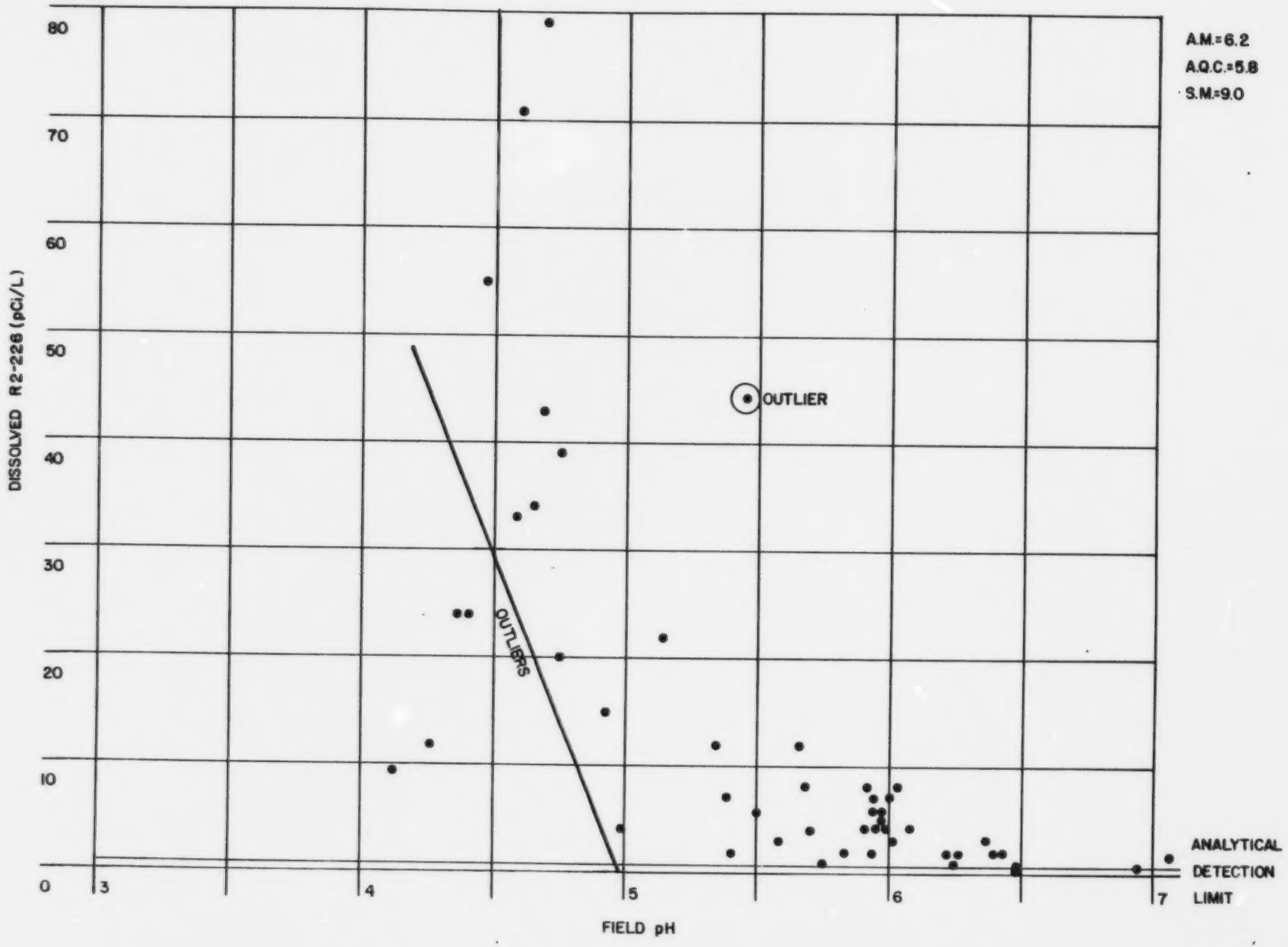


FIGURE A12.1 1980-1982 DATA N=193

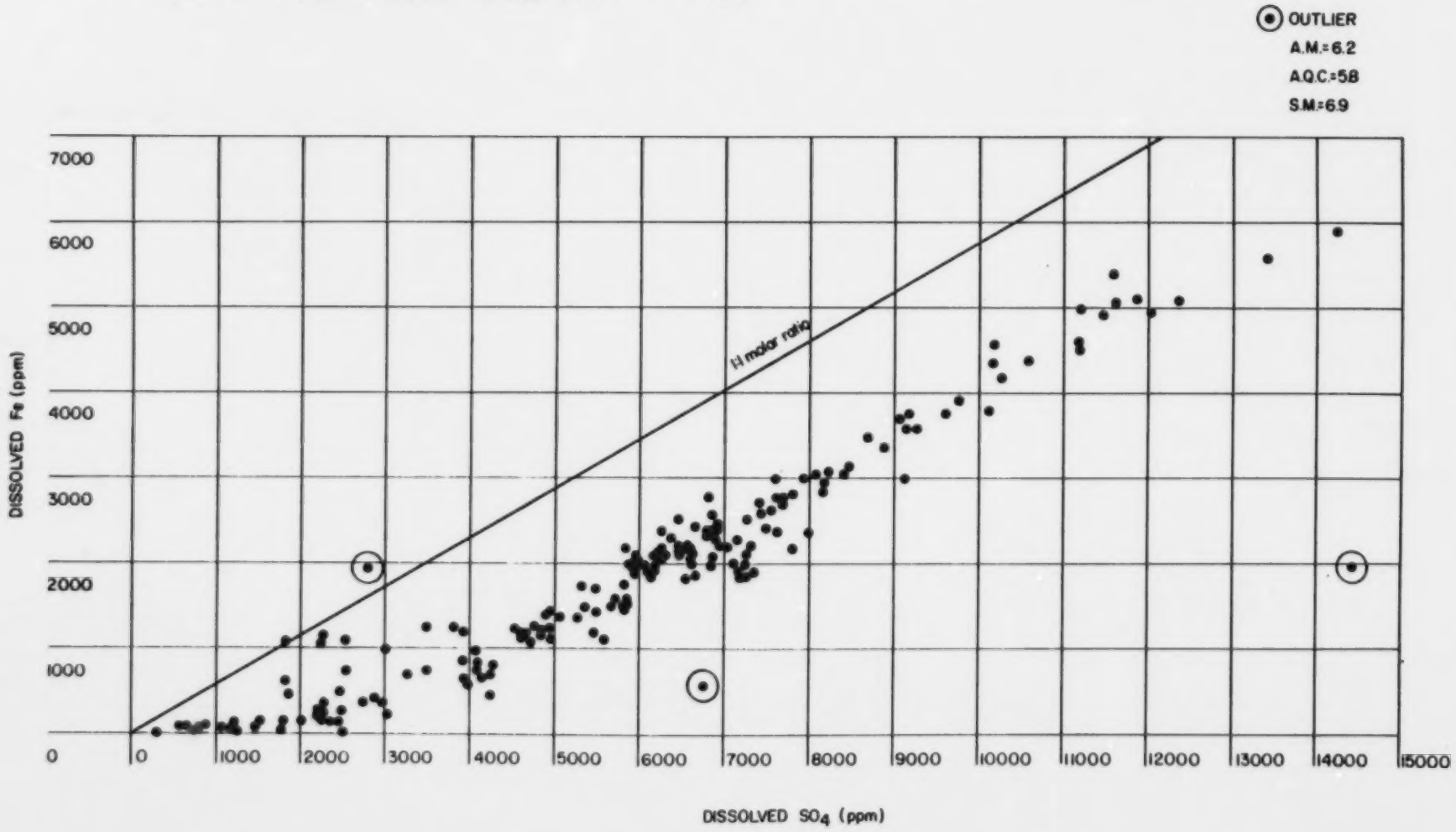


FIGURE 12.2 1983 DATA N=92

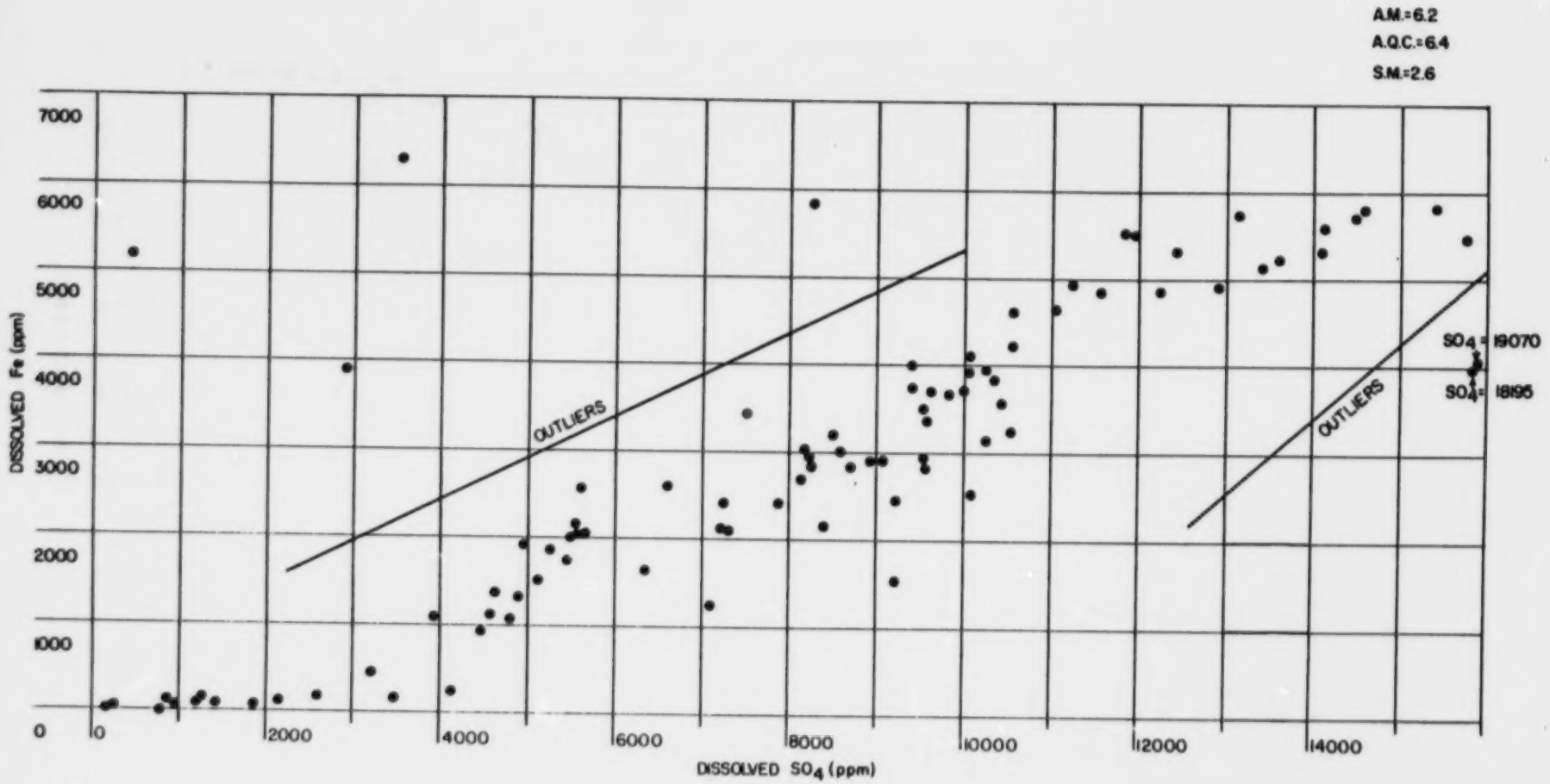


FIGURE A12.3 1984 DATA N=54

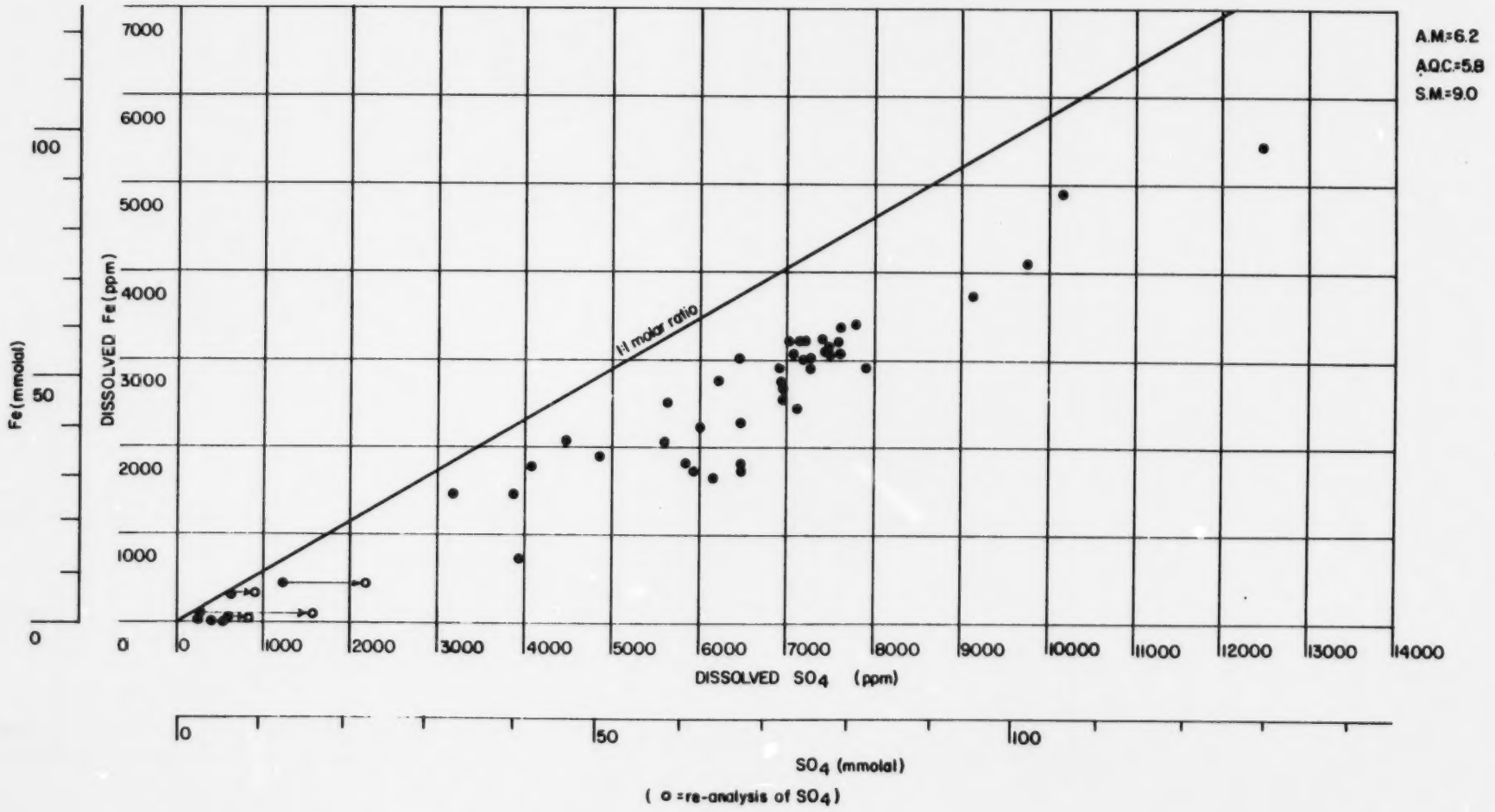


FIGURE A13.1 1980-1981 DATA N=81

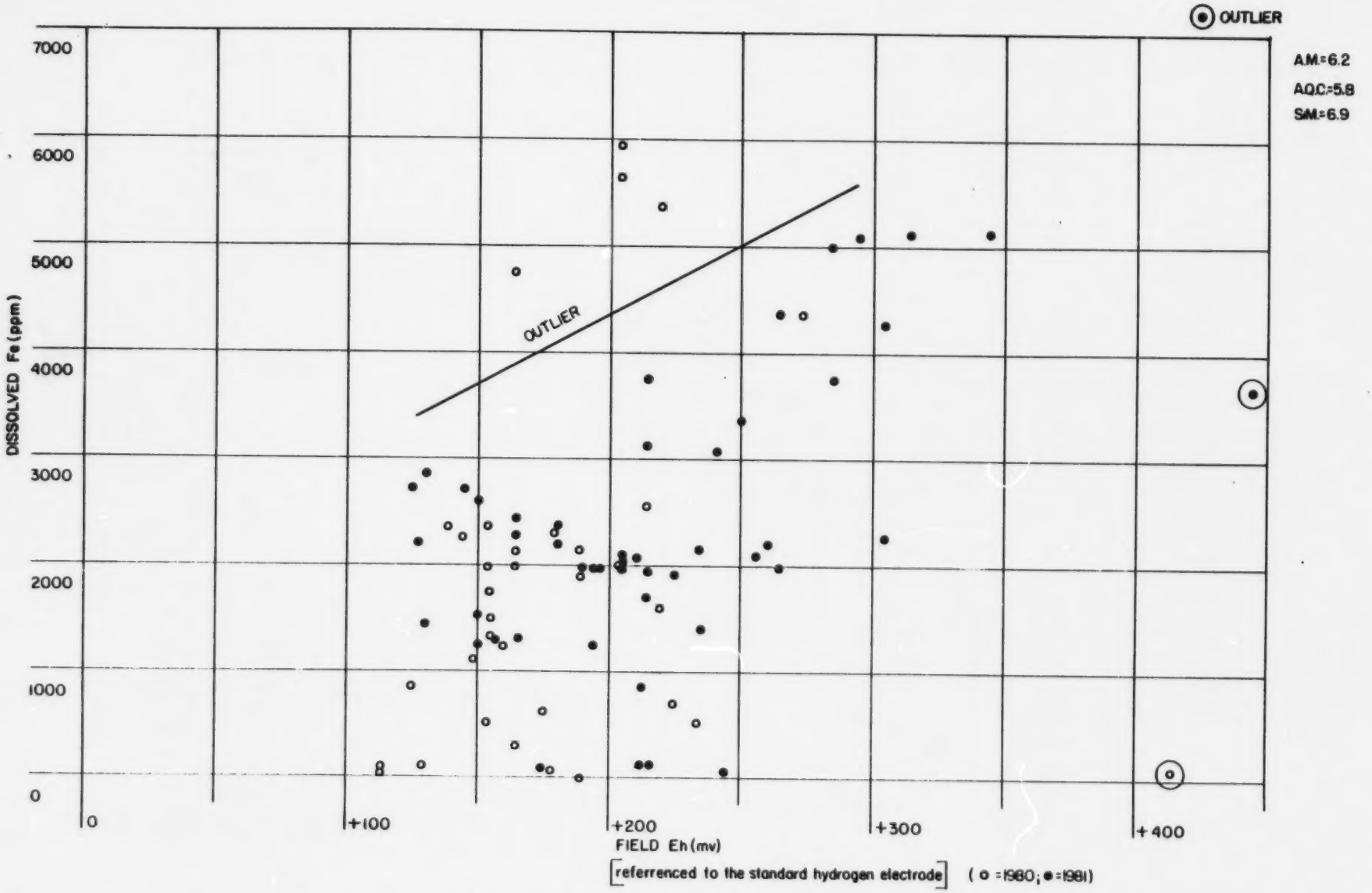


FIGURE A13.2 1983 DATA N=92

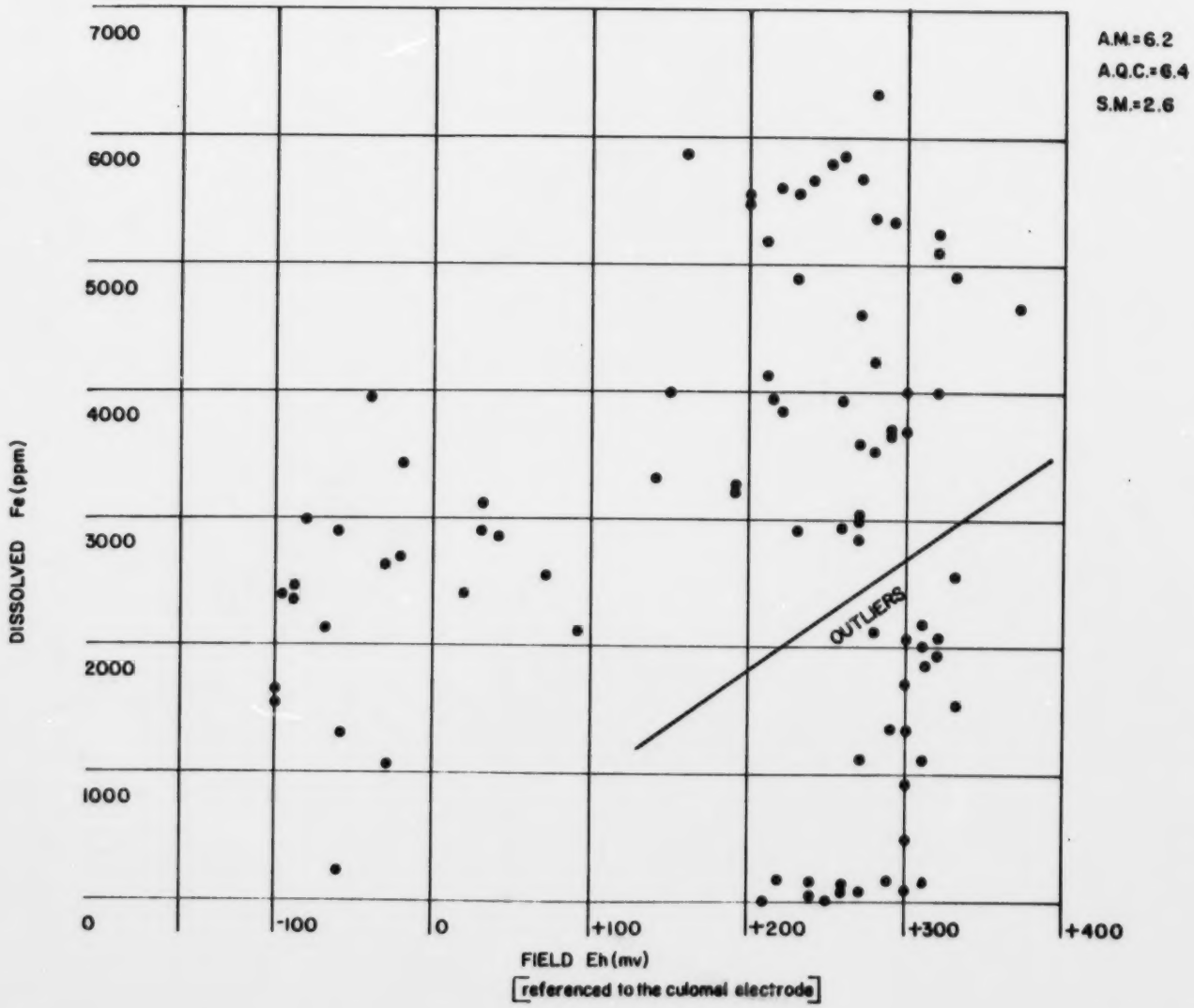


FIGURE A14.1 1980-1982 DATA N=194

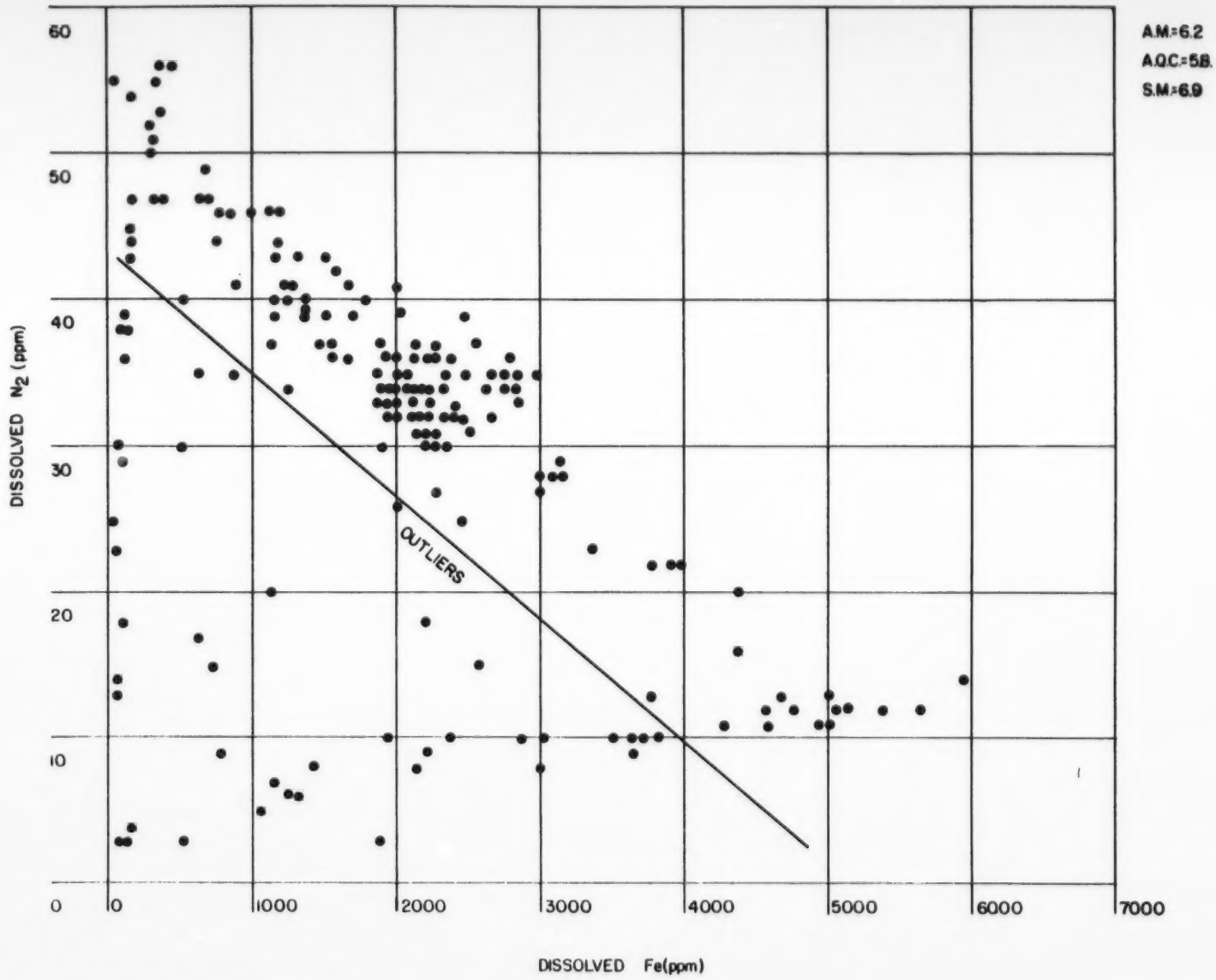


FIGURE 14.2 1984 DATA N=50

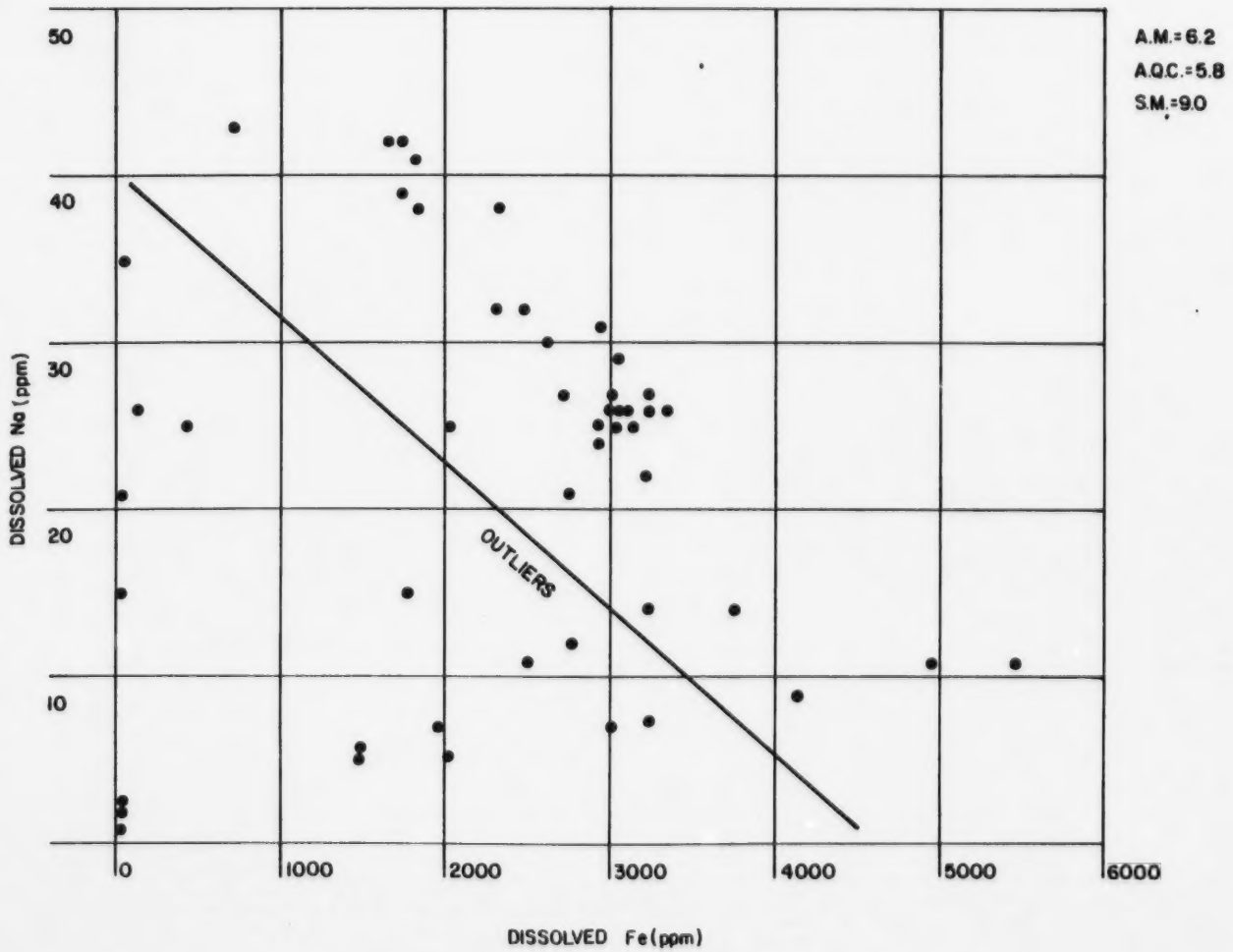


FIGURE A15.1 1981-1982 DATA N=76

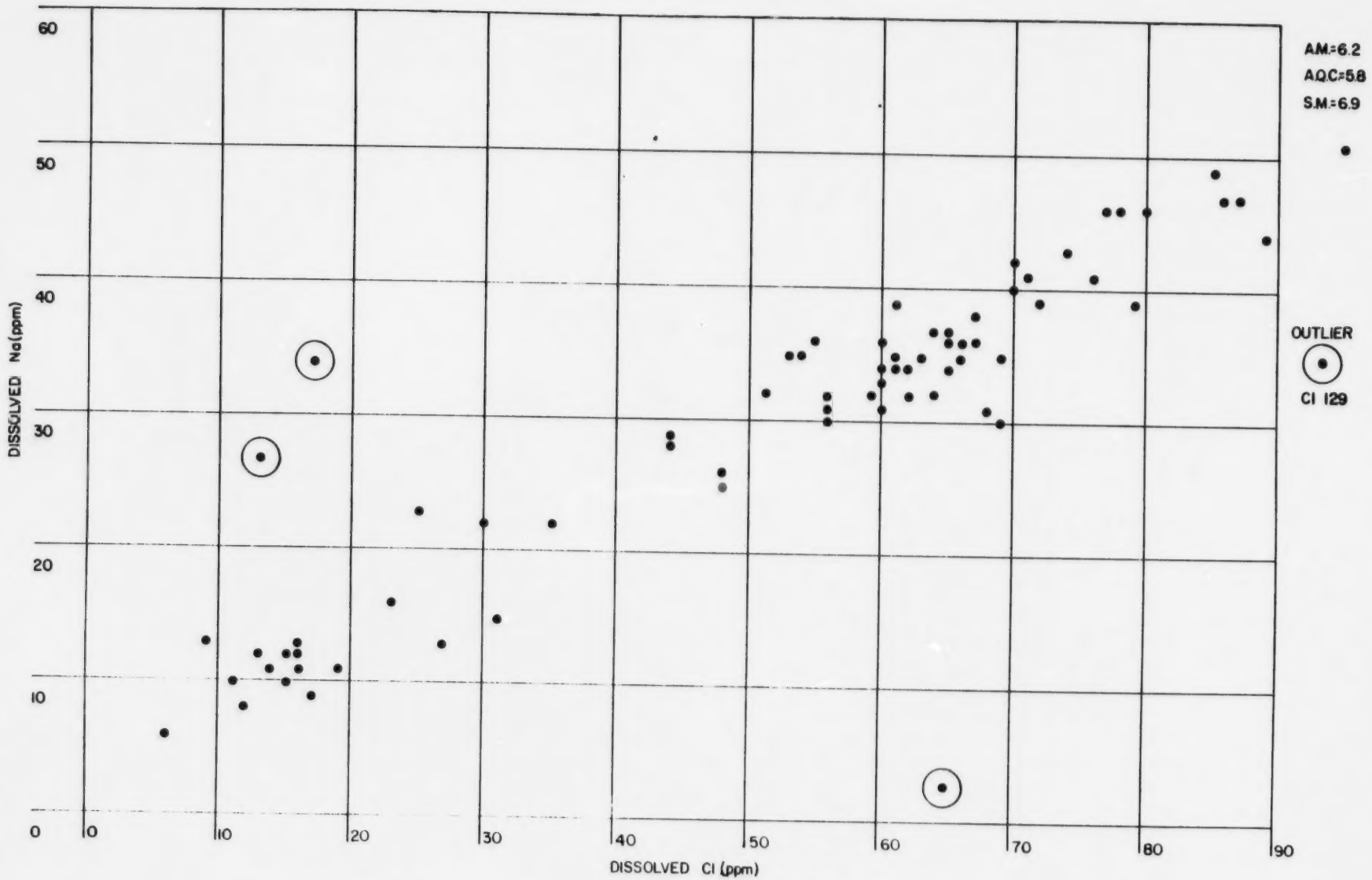


FIGURE A15.2 1984 DATA N=50

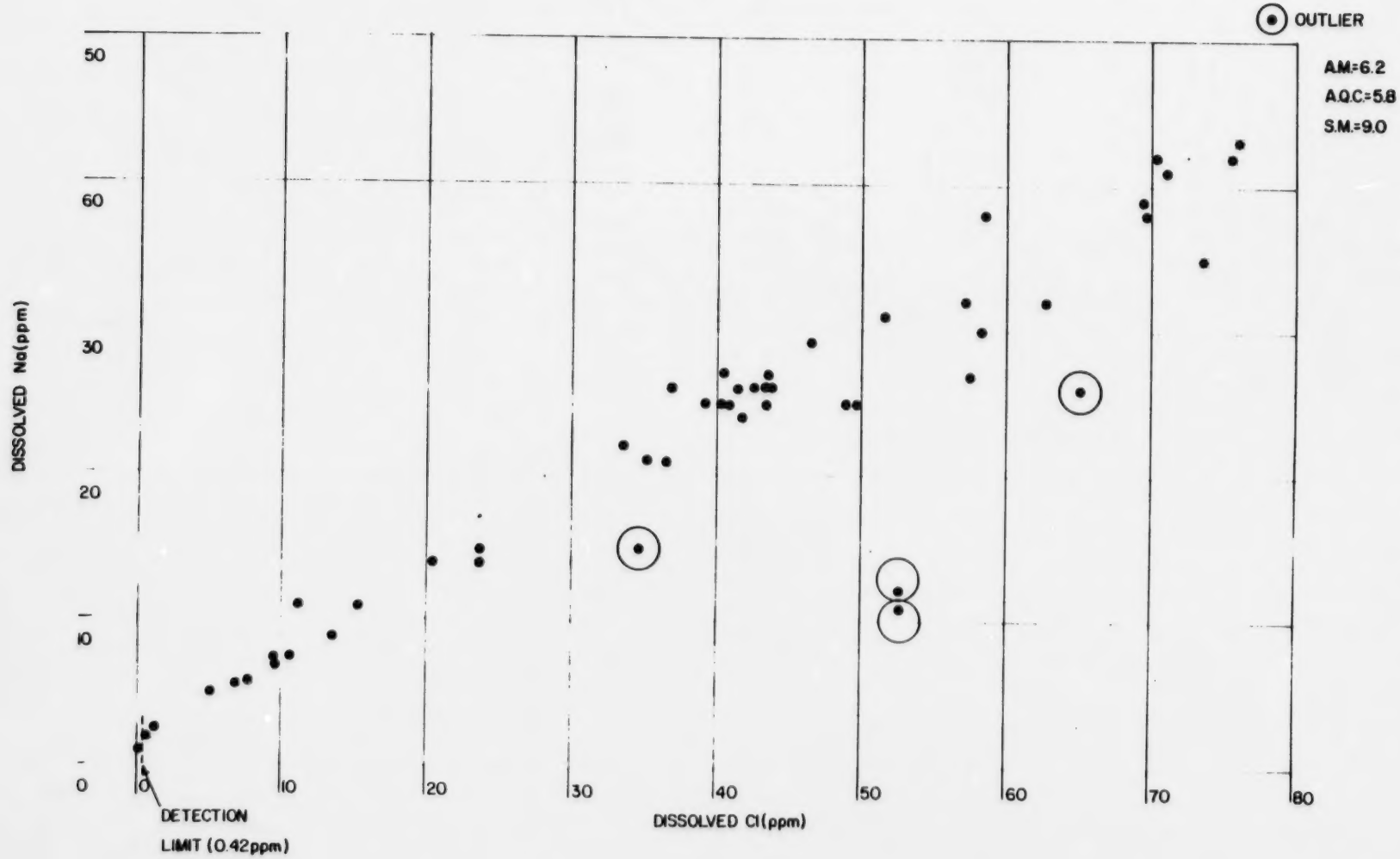


FIGURE 16.1 1980+1982 DATA N=120

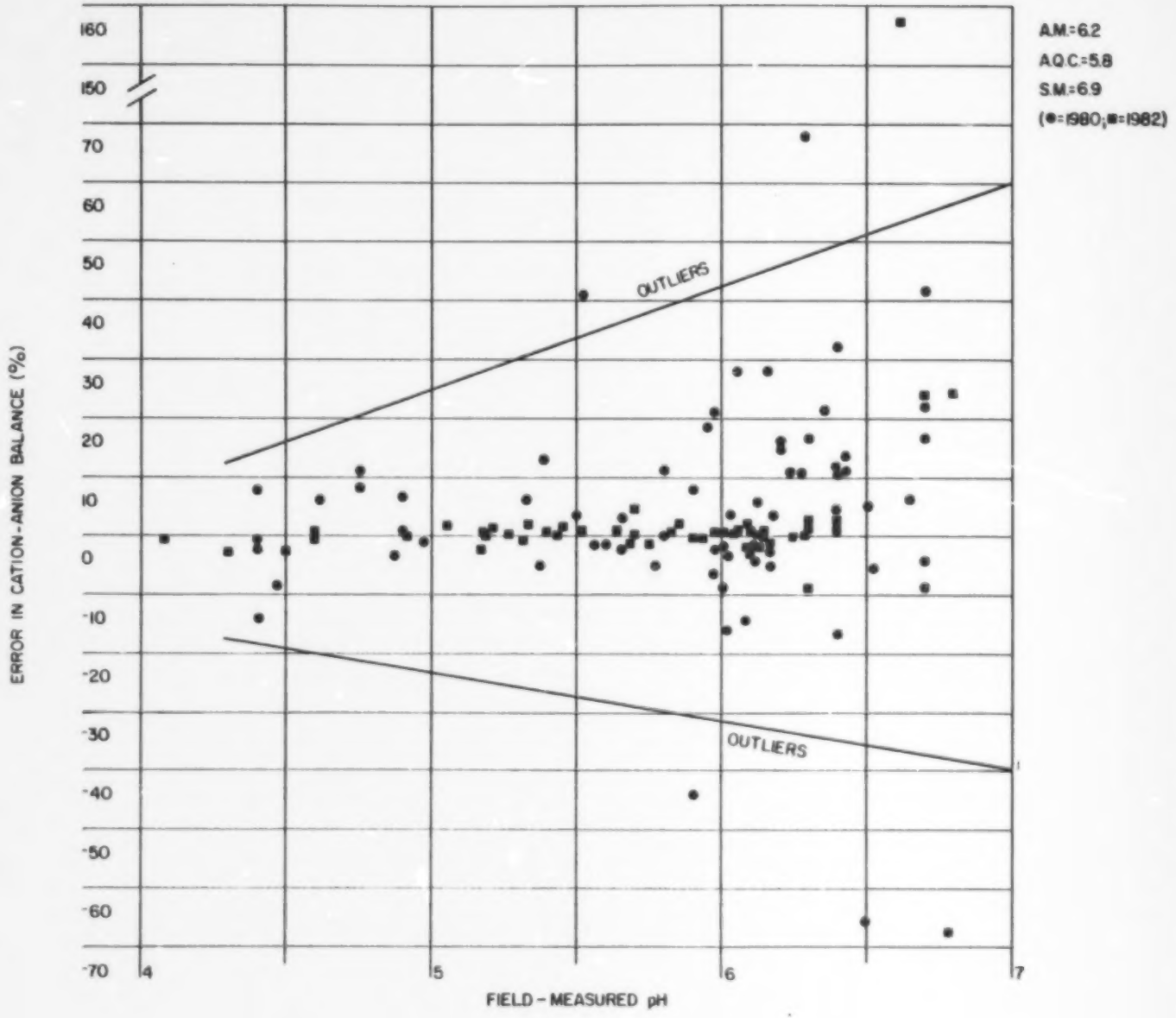


FIGURE A16.2 1983 DATA N=92

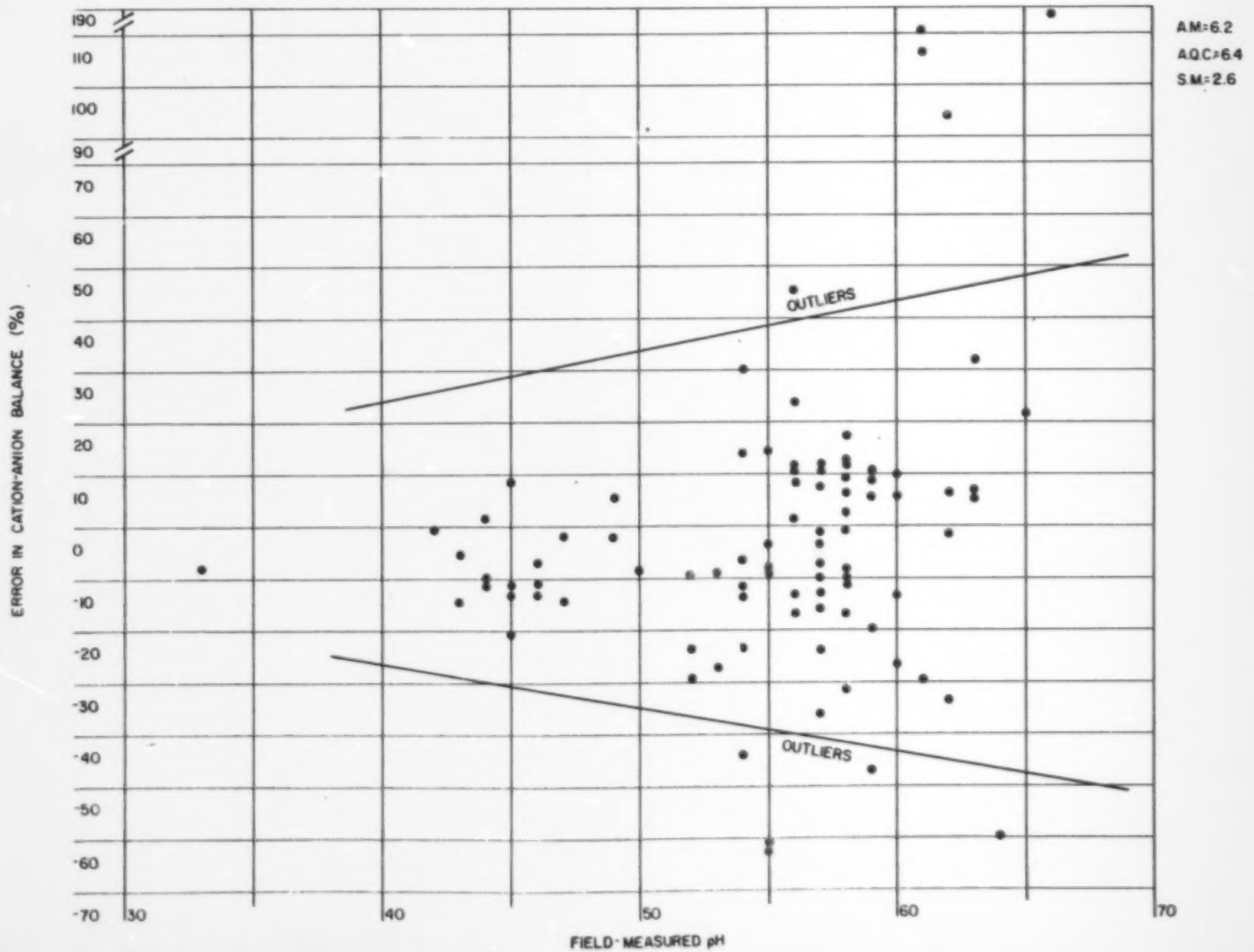


FIGURE A16.3 1984 DATA N=50

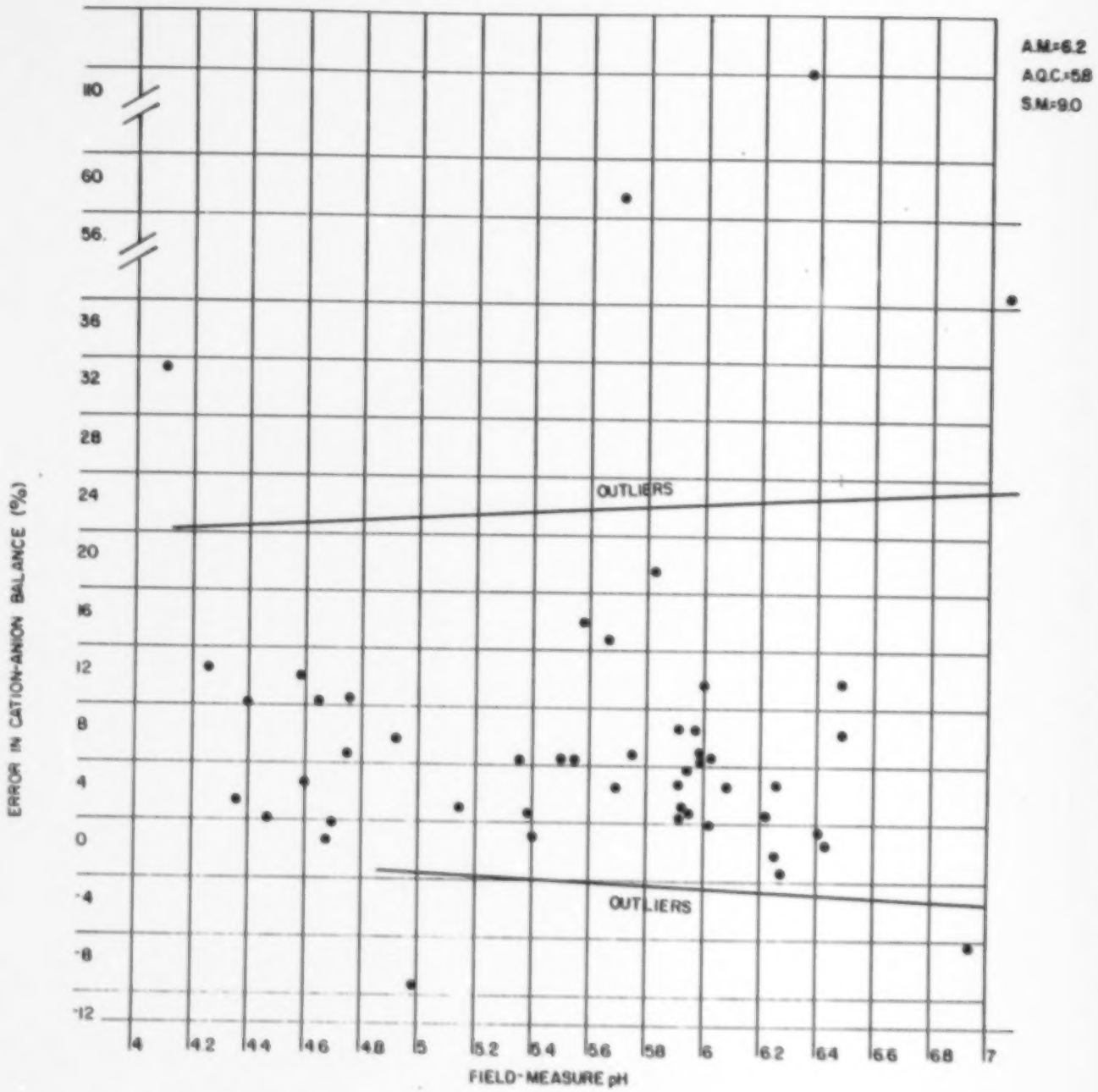


FIGURE A17.1 1979 DATA N=27

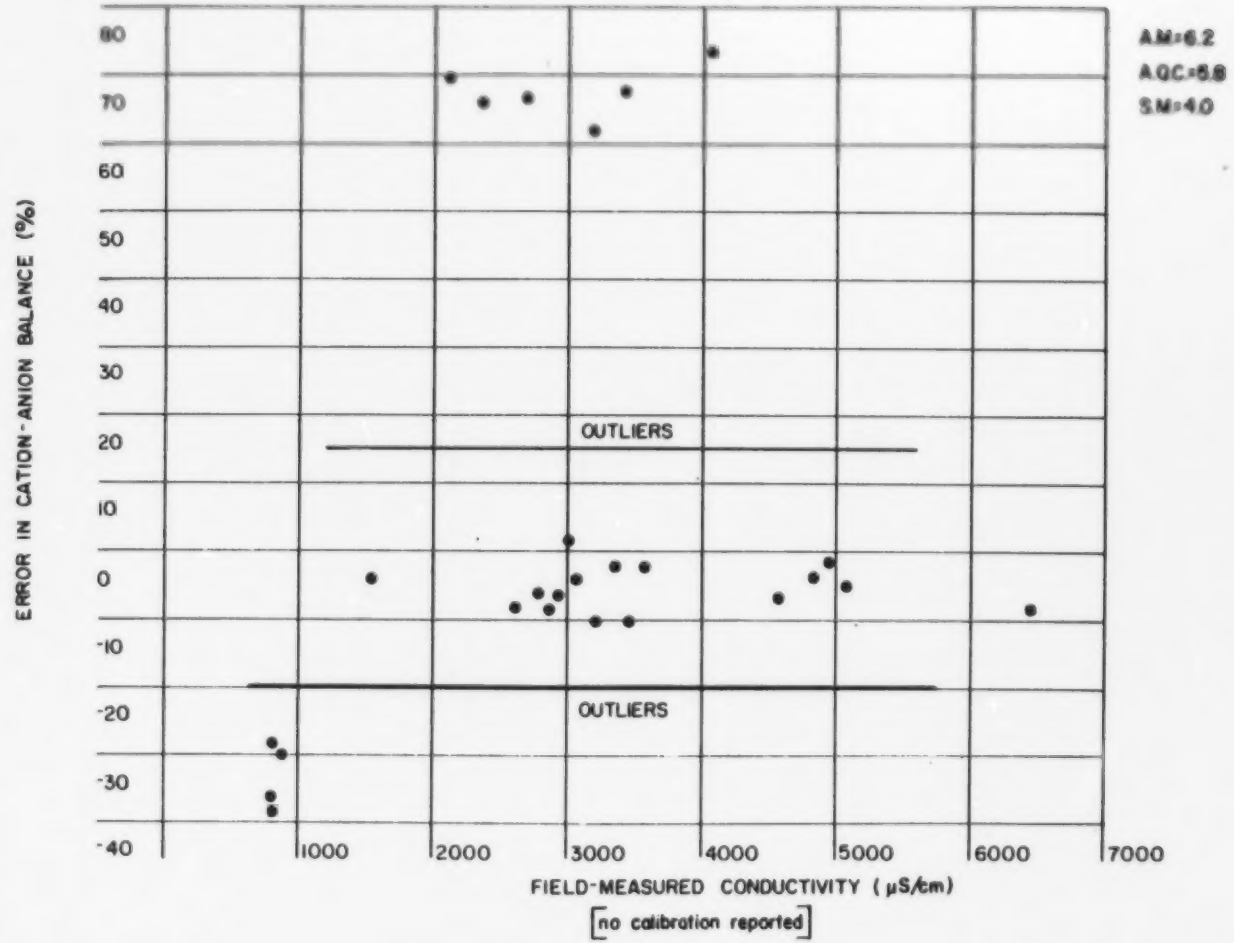


FIGURE A17.2 1980+1982 DATA N=121

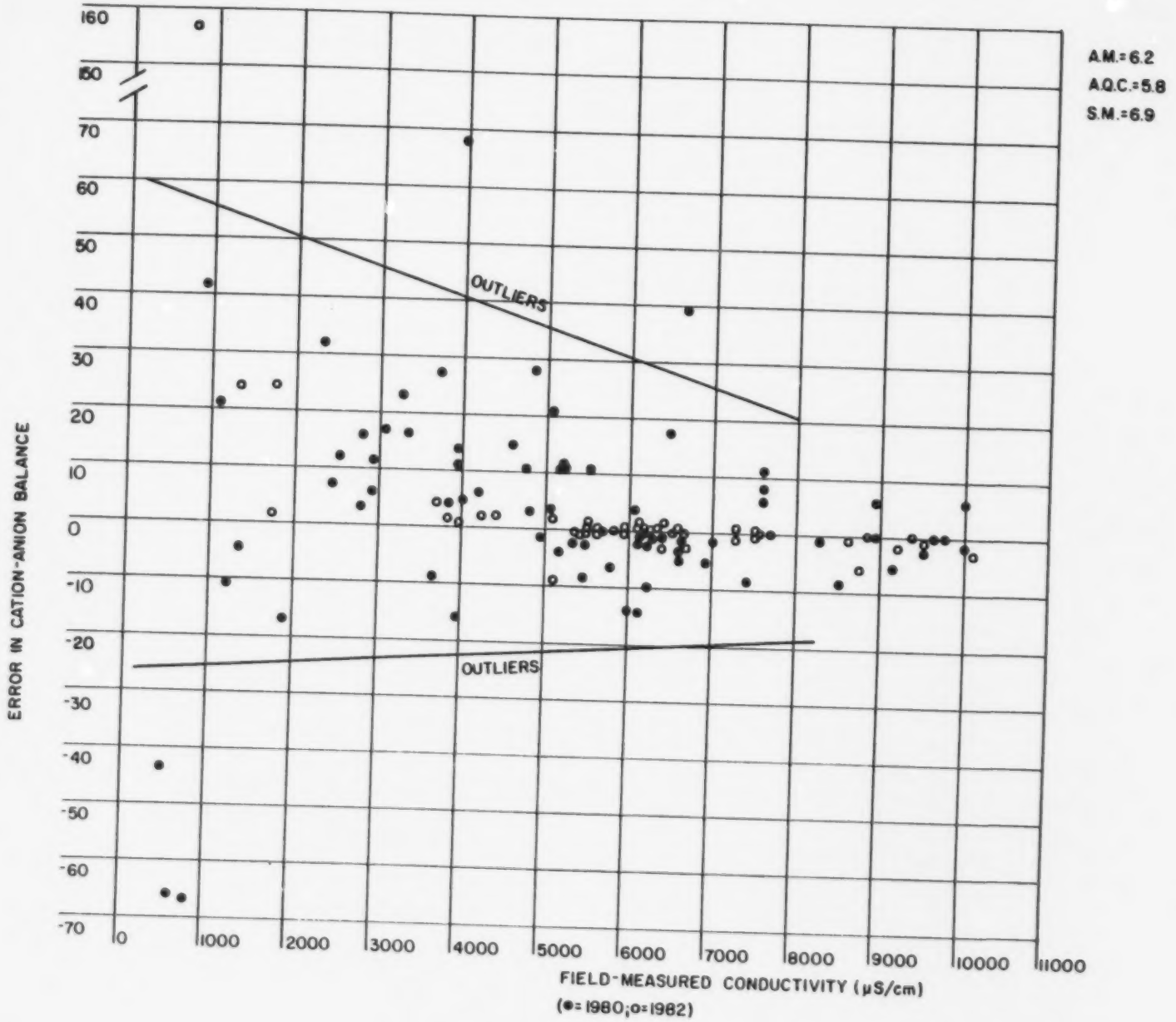


FIGURE A17.3 1983 DATA N=92

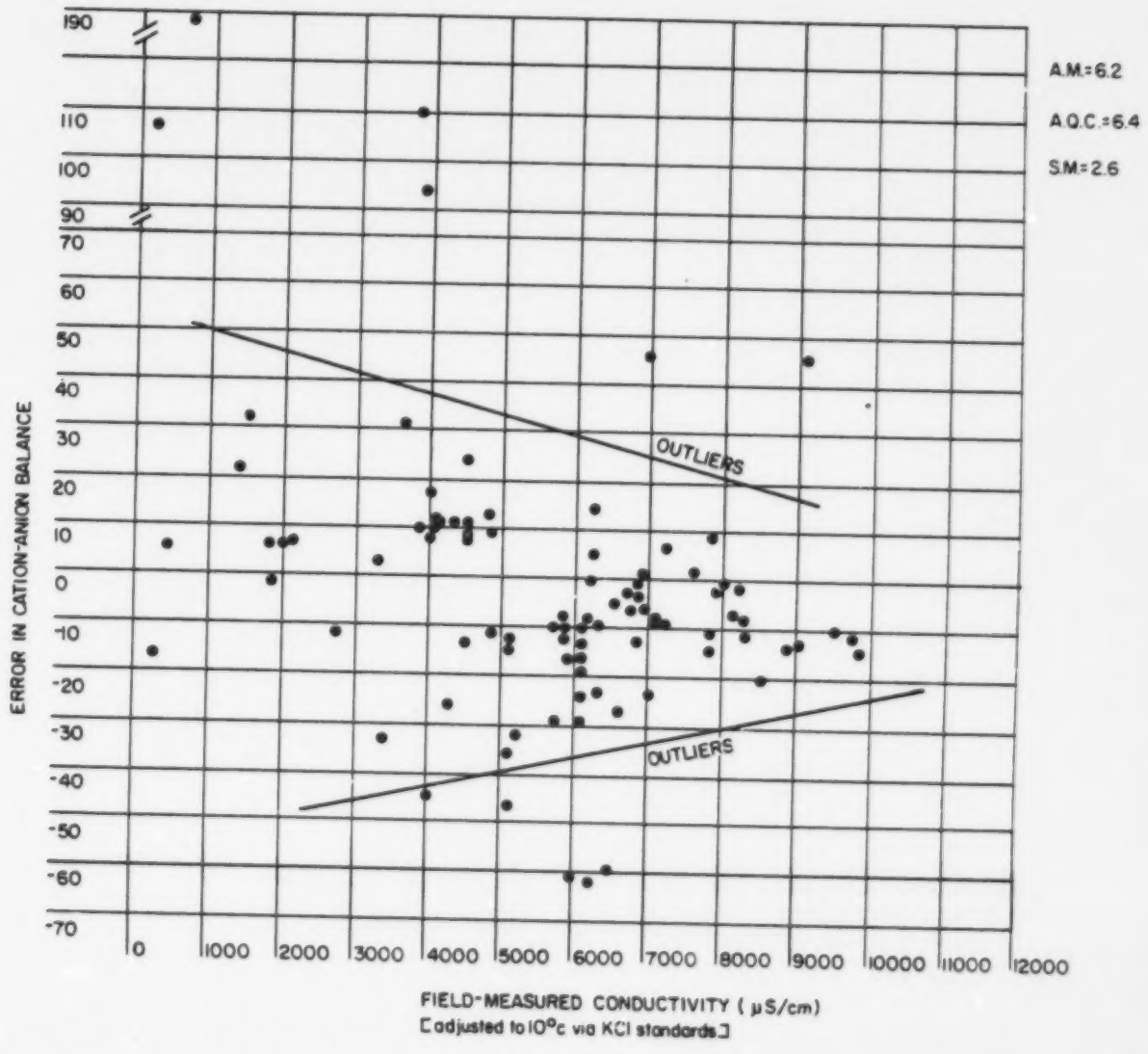


FIGURE A17.4 1984 DATA N=55

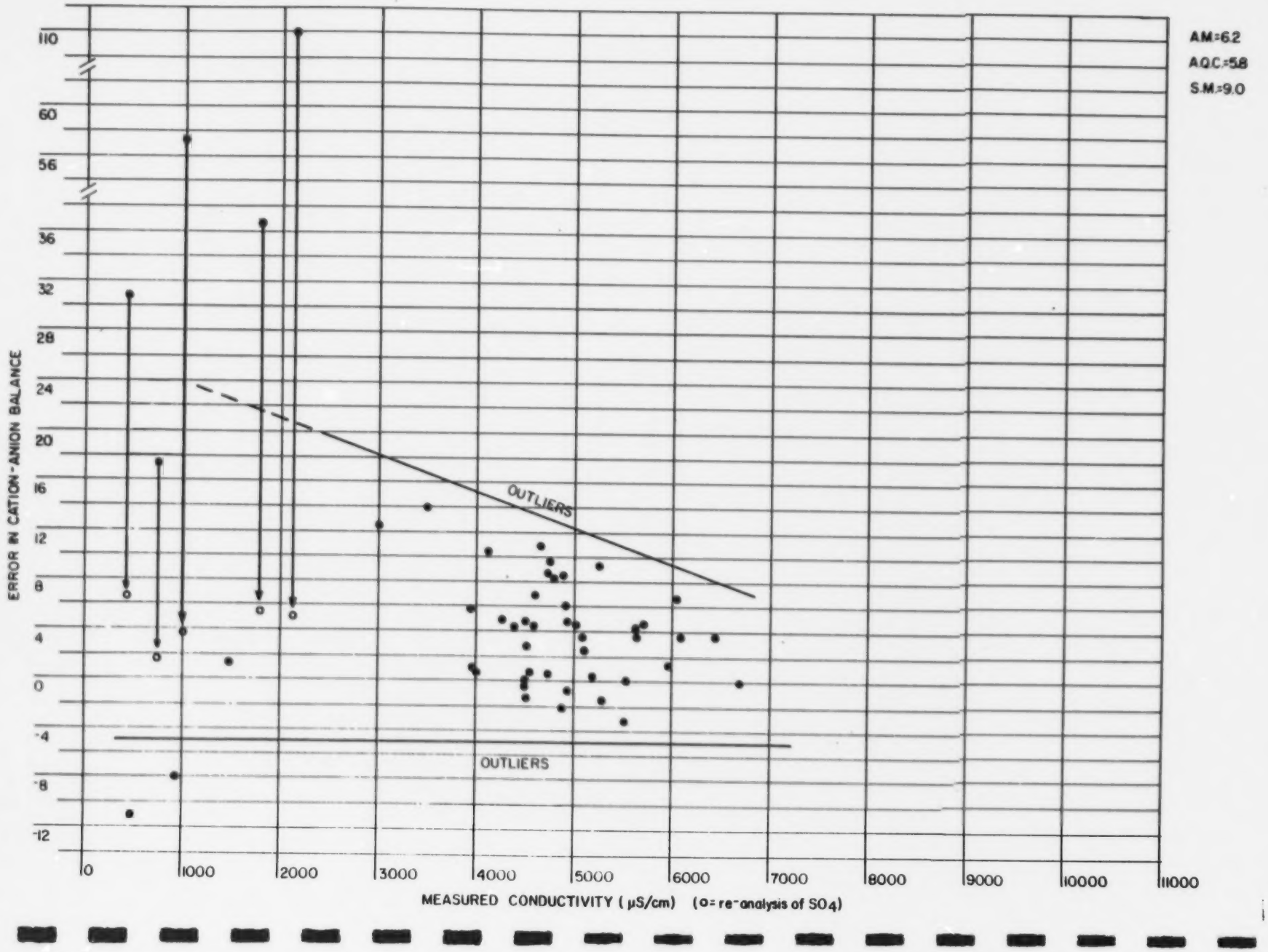


FIGURE A18: FREQUENCY DISTRIBUTIONS FOR RADIUM-226 IN SOIL AND TAILINGS

FREQUENCY BAR CHART OF RADIUM CONCENTRATIONS OVER SETS
SET=CSOILS

MIDPOINT CRA	FREQ	CUM. FREQ	PERCENT	CUM. PERCENT
0.1	8	8	29.63	29.63
20.1	15	23	55.56	85.19
40.1	3	26	11.11	96.30
140.1	(1)	27	3.70	100.00

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
FREQUENCY

FREQUENCY BAR CHART OF RADIUM CONCENTRATIONS OVER SETS
SET=BTAILS

MIDPOINT CRA	FREQ	CUM. FREQ	PERCENT	CUM. PERCENT
0.1	13	13	30.23	30.23
20.1	10	23	23.26	53.49
40.1	6	29	13.95	67.44
60.1	6	35	13.95	81.40
80.1	1	36	2.33	83.72
100.1	1	37	2.33	86.05
120.1	1	38	2.33	88.37
140.1	2	40	4.65	93.02
200.1	3	43	6.98	100.00

1 2 3 4 5 6 7 8 9 10 11 12 13
FREQUENCY

FREQUENCY BAR CHART OF RADIUM CONCENTRATIONS OVER SETS
SET=DTAILS

MIDPOINT CRA	FREQ	CUM. FREQ	PERCENT	CUM. PERCENT
0.1	10	10	13.51	13.51
20.1	32	42	43.24	56.76
40.1	15	57	20.27	77.03
60.1	4	61	5.41	82.43
80.1	5	66	6.76	89.19
100.1	1	67	1.35	90.54
120.1	2	69	2.70	93.24
140.1	2	71	2.70	95.95
160.1	2	73	2.70	98.65
260.1	(1)	74	1.35	100.00

2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32
FREQUENCY

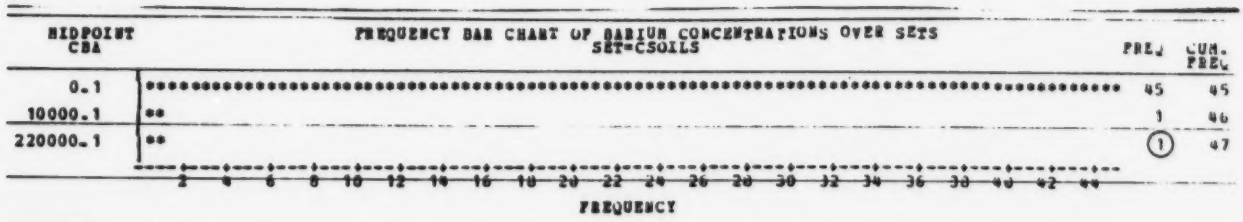
FREQUENCY BAR CHART OF RADIUM CONCENTRATIONS OVER SETS
SET=UTAILS

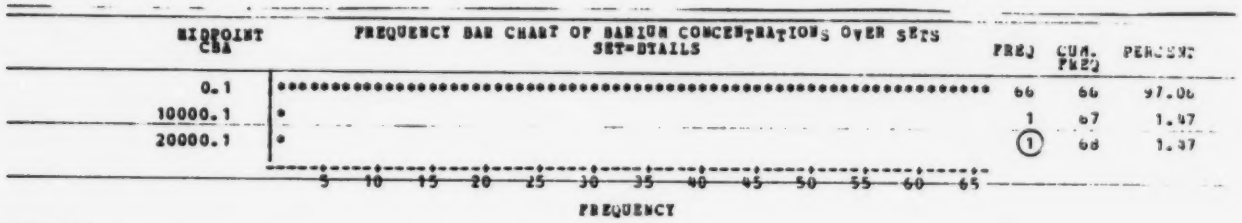
MIDPOINT CRA	FREQ	CUM. FREQ	PERCENT	CUM. PERCENT
0.1	8	8	14.81	14.81
20.1	7	15	12.96	27.78
40.1	5	20	9.26	37.04
60.1	13	33	24.07	61.11
80.1	7	40	12.96	74.07
100.1	4	44	7.41	81.48
120.1	4	48	7.41	88.89
160.1	1	49	1.85	90.74
180.1	1	50	1.85	92.59
200.1	1	51	1.85	94.44
220.1	2	53	3.70	98.15
240.1	1	54	1.85	100.00

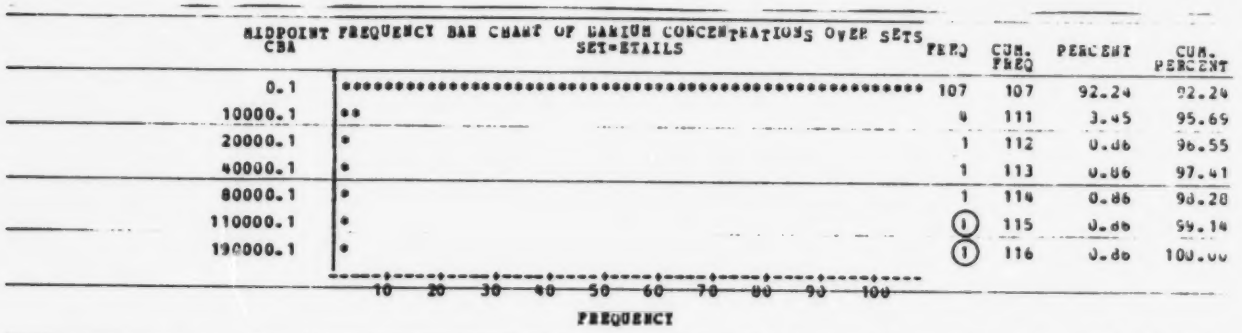
1 2 3 4 5 6 7 8 9 10 11 12 13
FREQUENCY

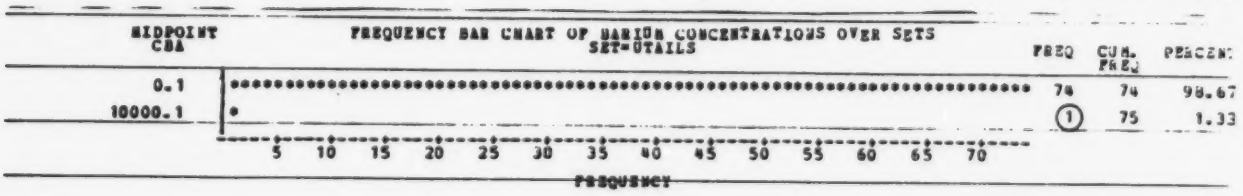
NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A19: FREQUENCY DISTRIBUTIONS FOR BARIUM IN SOIL AND TAILINGS


MIDPOINT CBA
FREQUENCY BAR CHART OF BARIUM CONCENTRATIONS OVER SETS
SET=CSOILS
FREQ
CUM. FREQ
0.1 45 45
10000.1 1 46
220000.1 1 47
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44
FREQUENCY







NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A20: FREQUENCY DISTRIBUTIONS FOR CALCIUM IN SOIL AND TAILINGS

MIDPOINT CCA	FREQUENCY BAR CHART OF CALCIUM CONCENTRATIONS OVER SETS SET=CSOILS	FREQ	CUM. FREQ	PERCENT	CUM. PERCENT
0.1	**********	11	11	20.75	20.75
10000.1	**********	33	44	62.26	83.02
20000.1	*******	7	51	13.21	96.23
30000.1	**	1	52	1.89	98.11
50000.1	**	(1)	53	1.89	100.00

2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32

FREQUENCY

MIDPOINT CCA	FREQUENCY BAR CHART OF CALCIUM CONCENTRATIONS OVER SETS SET=BTAILS	FREQ	CUM. FREQ	PERCENT	CUM. PERCENT
0.1	**********	6	6	8.22	8.22
10000.1	******	3	9	4.11	12.33
20000.1	**********	10	19	13.70	26.03
30000.1	**********	32	51	43.84	69.86
40000.1	**********	18	69	24.66	94.52
50000.1	****	2	71	2.74	97.26
60000.1	**	1	72	1.37	98.63
80000.1	**	(1)	73	1.37	100.00

2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32

FREQUENCY

MIDPOINT CCA	FREQUENCY BAR CHART OF CALCIUM CONCENTRATIONS OVER SETS SET=ETAILS	FREQ	CUM. FREQ	PERCENT	CUM. PERCENT
0.1	**********	61	61	64.21	64.21
10000.1	**********	19	80	20.00	84.21
20000.1	******	6	86	6.32	90.53
30000.1	**	2	88	2.11	92.63
40000.1	**	2	90	2.11	94.74
50000.1	***	3	93	3.16	97.89
190000.1	*	1	94	1.05	98.95
610000.1	*	(1)	95	1.05	100.00

5 10 15 20 25 30 35 40 45 50 55 60

FREQUENCY

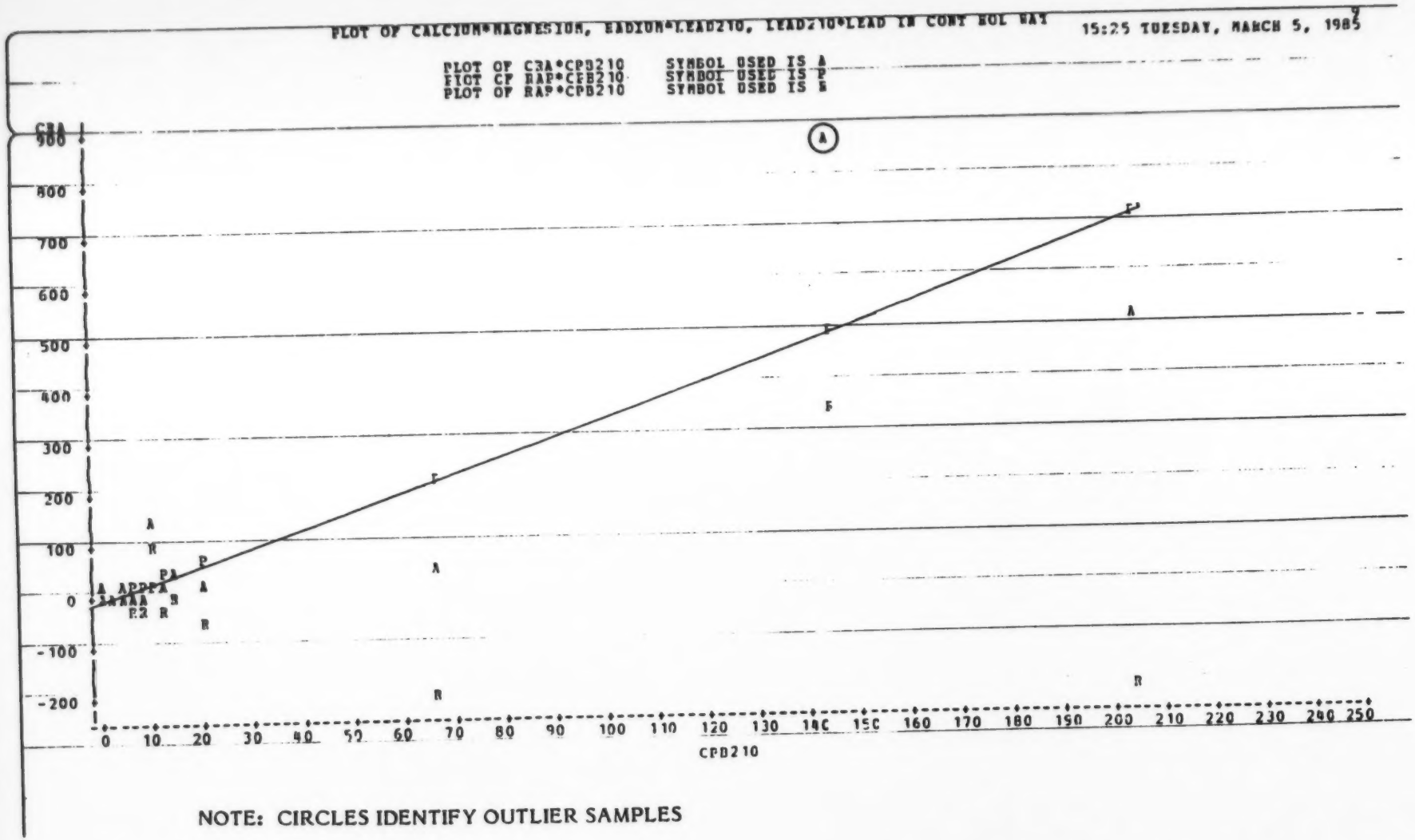
MIDPOINT CCA	FREQUENCY BAR CHART OF CALCIUM CONCENTRATIONS OVER SETS SET=GTAILS	FREQ	CUM. FREQ	PERCENT	CUM. PERCENT
0.1	**********	7	7	9.33	9.33
10000.1	**********	33	40	44.00	53.33
20000.1	**********	8	48	10.67	64.00
30000.1	**********	10	58	13.33	77.33
40000.1	**********	7	65	9.33	86.67
50000.1	**********	7	72	9.33	96.00
60000.1	****	2	74	2.67	98.67
70000.1	**	1	75	1.33	100.00

2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32

FREQUENCY

NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.1: RADIUM-226 VS. LEAD-210 IN CONTROL WATER



NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.2: RADIUM-226 VS. LEAD-210 IN CONTROL SOIL

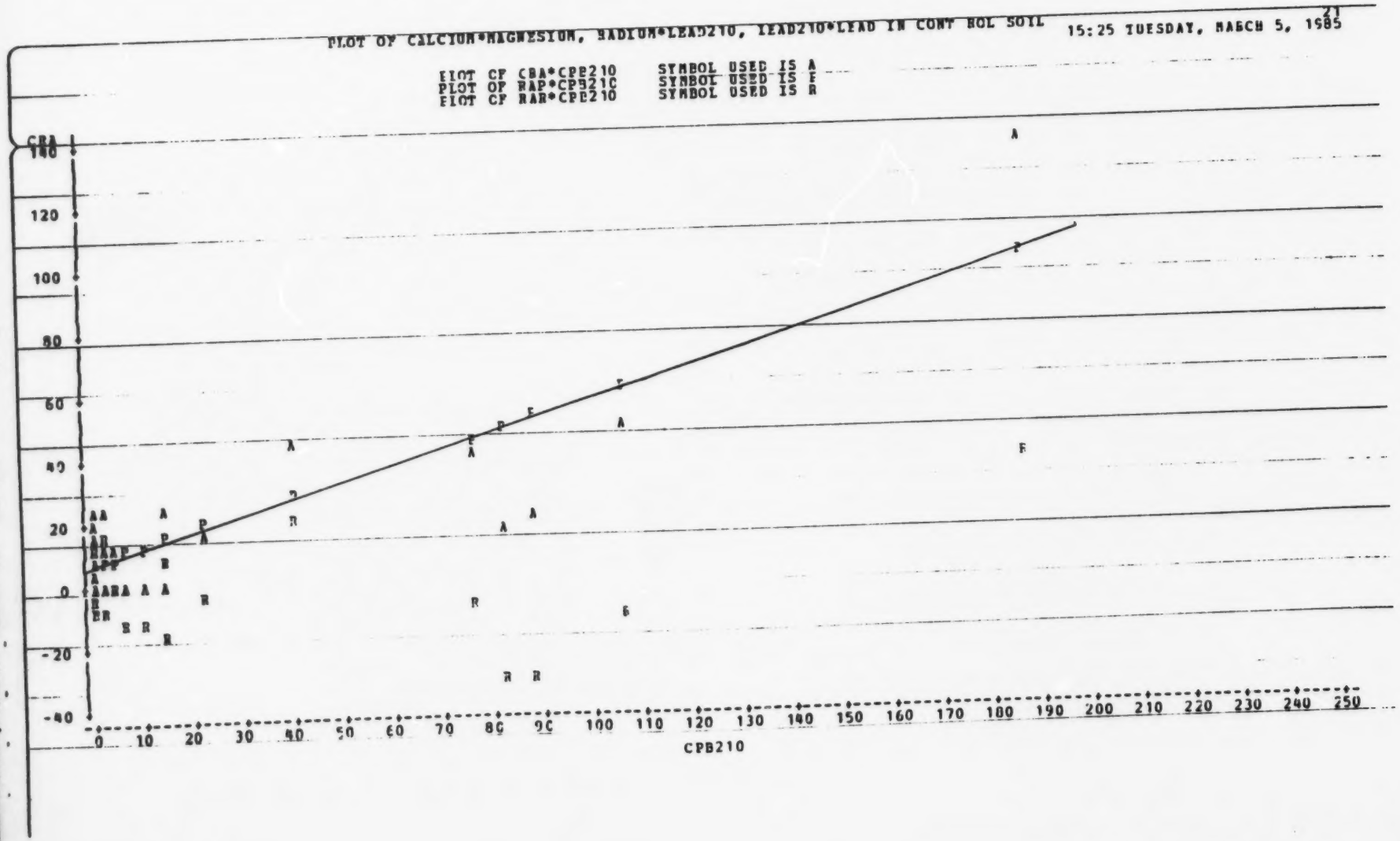
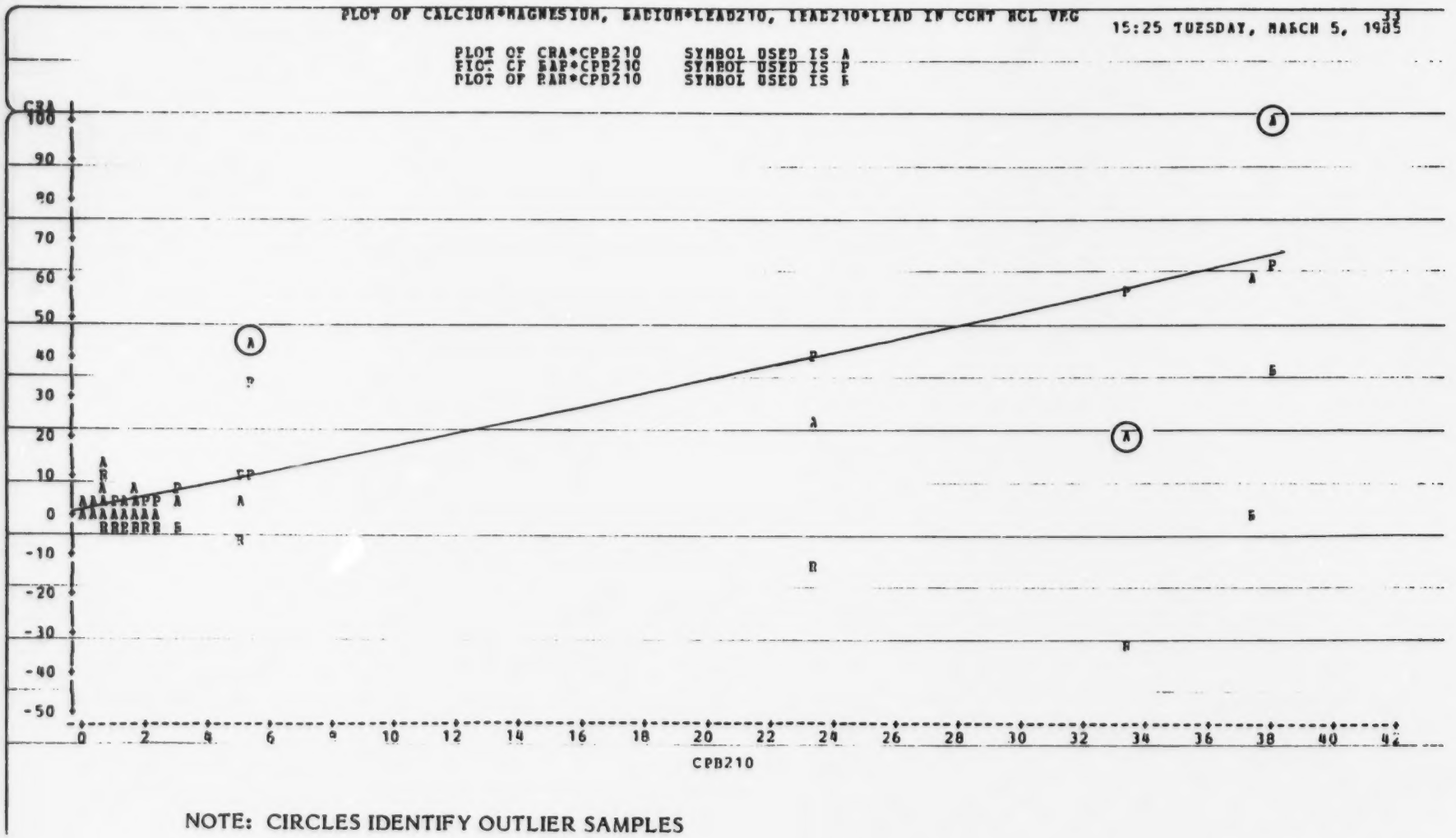


FIGURE A21.3: RADIUM-226 VS. LEAD-210 IN CONTROL VEGETATION



NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.4: RADIUM-226 VS. LEAD-210 IN BANCROFT WATER

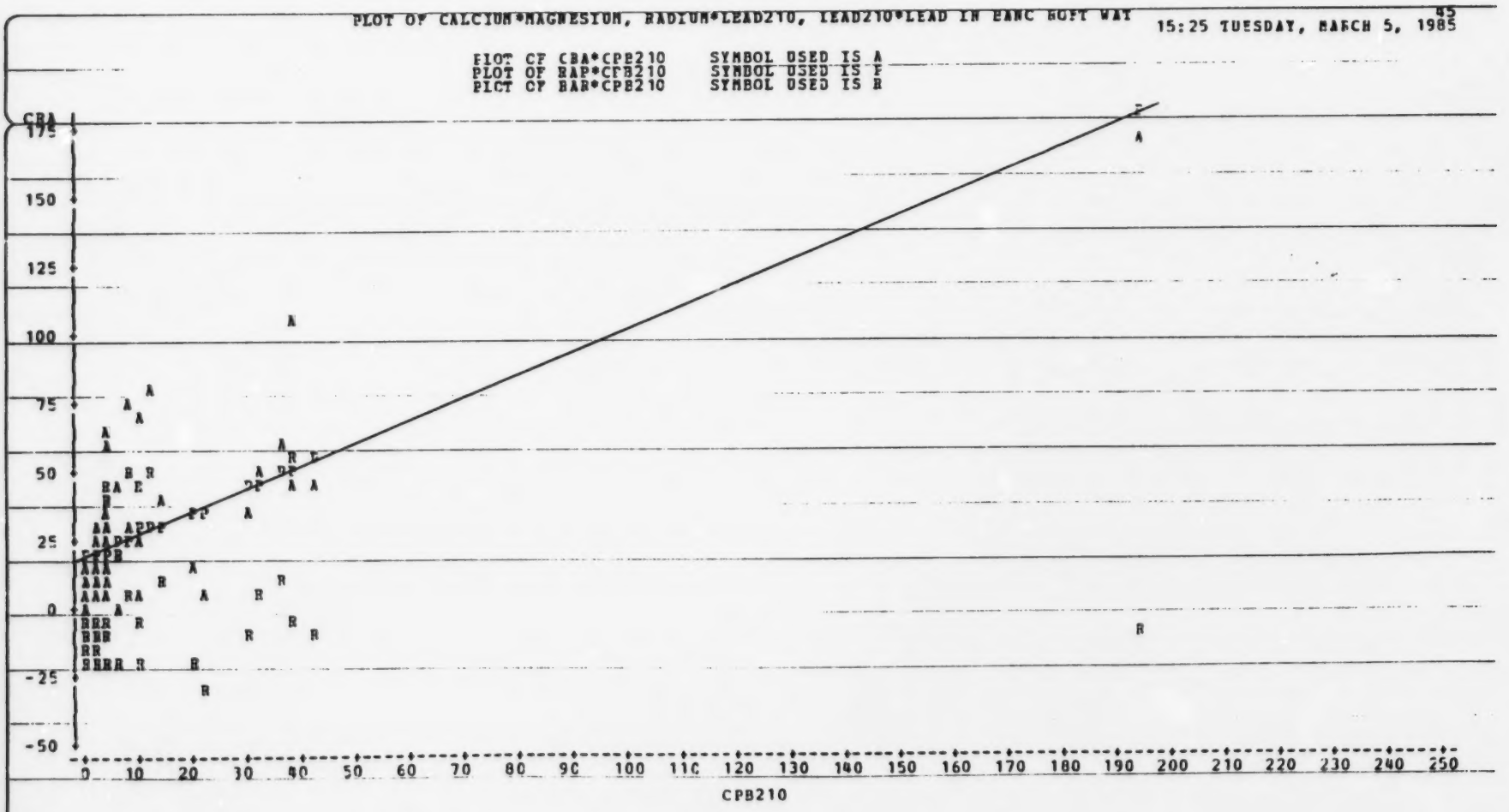
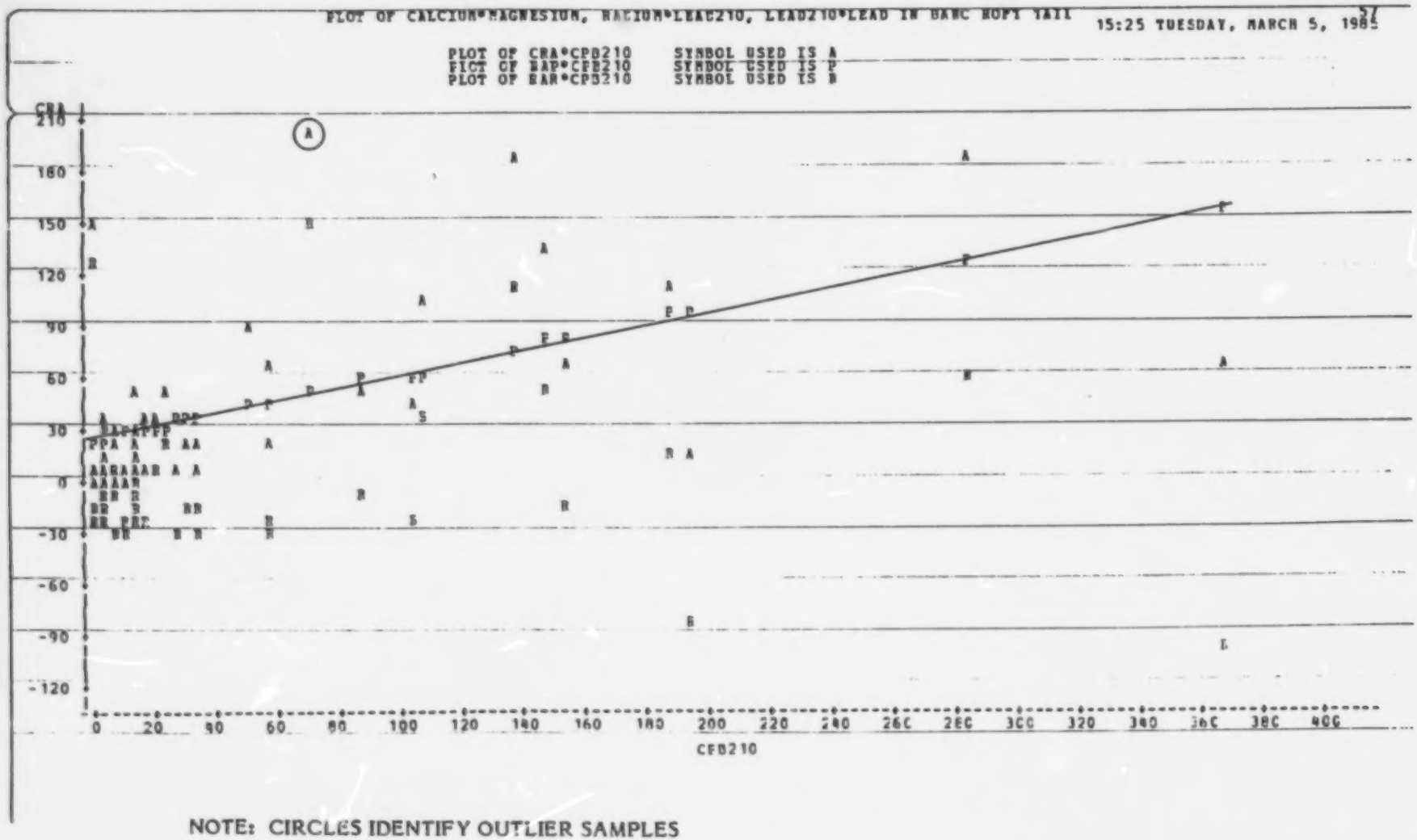
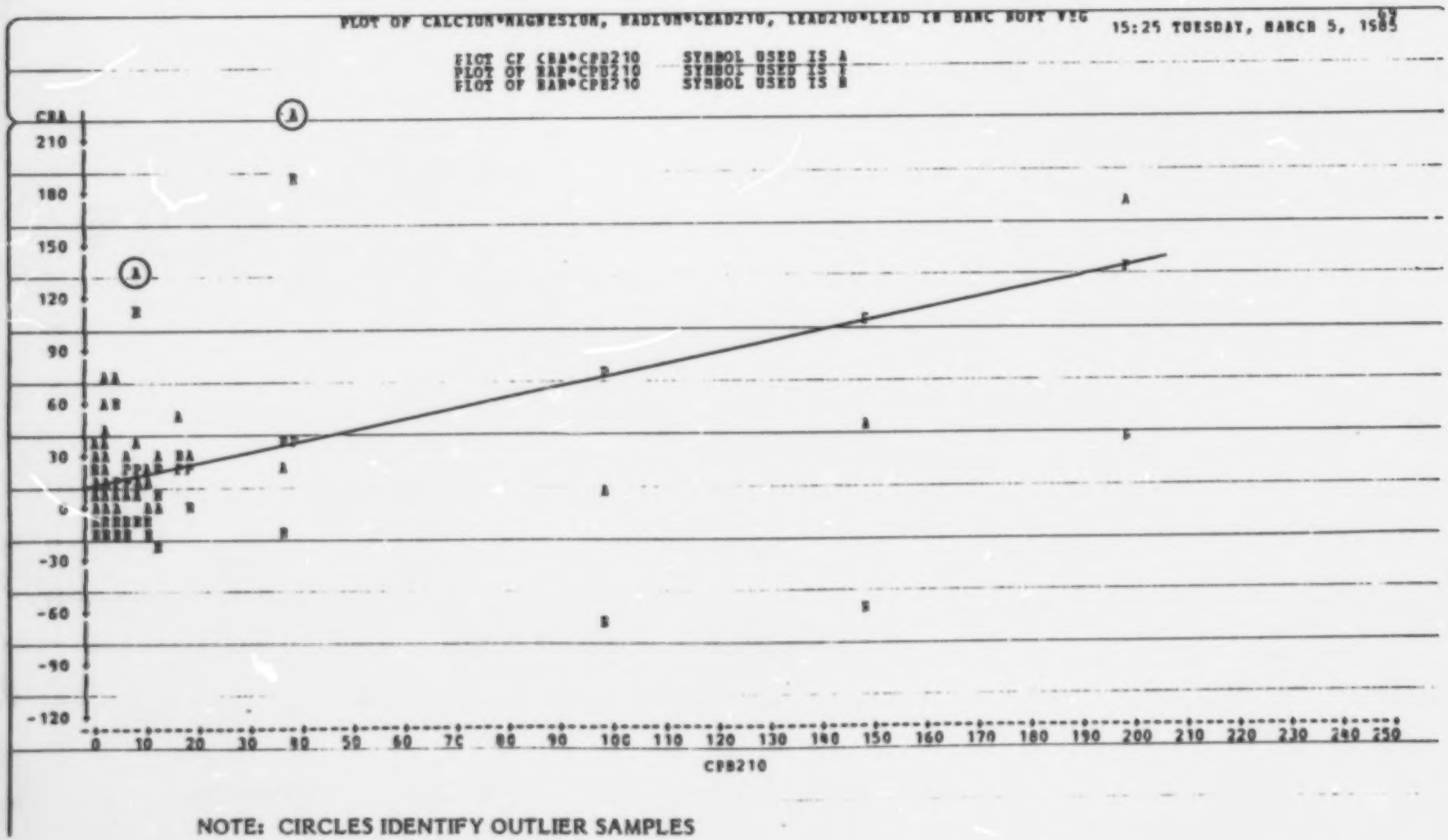

PLOT OF CALCIUM*MAGNESIUM, RADIUM*LEAD210, LEAD210*LEAD IN BANC HOFT WAT
15:25 TUESDAY, MARCH 5, 1985
PLOT OF CBA*CPB210 SYMBOL USED IS A
PLOT OF BAP*CPB210 SYMBOL USED IS F
PLOT OF BAR*CPB210 SYMBOL USED IS R
CBA
150
125
100
75
50
25
0
-25
-50
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250
CPB210

FIGURE A21.5: RADIUM-226 VS. LEAD-210 IN BANCROFT TAILINGS



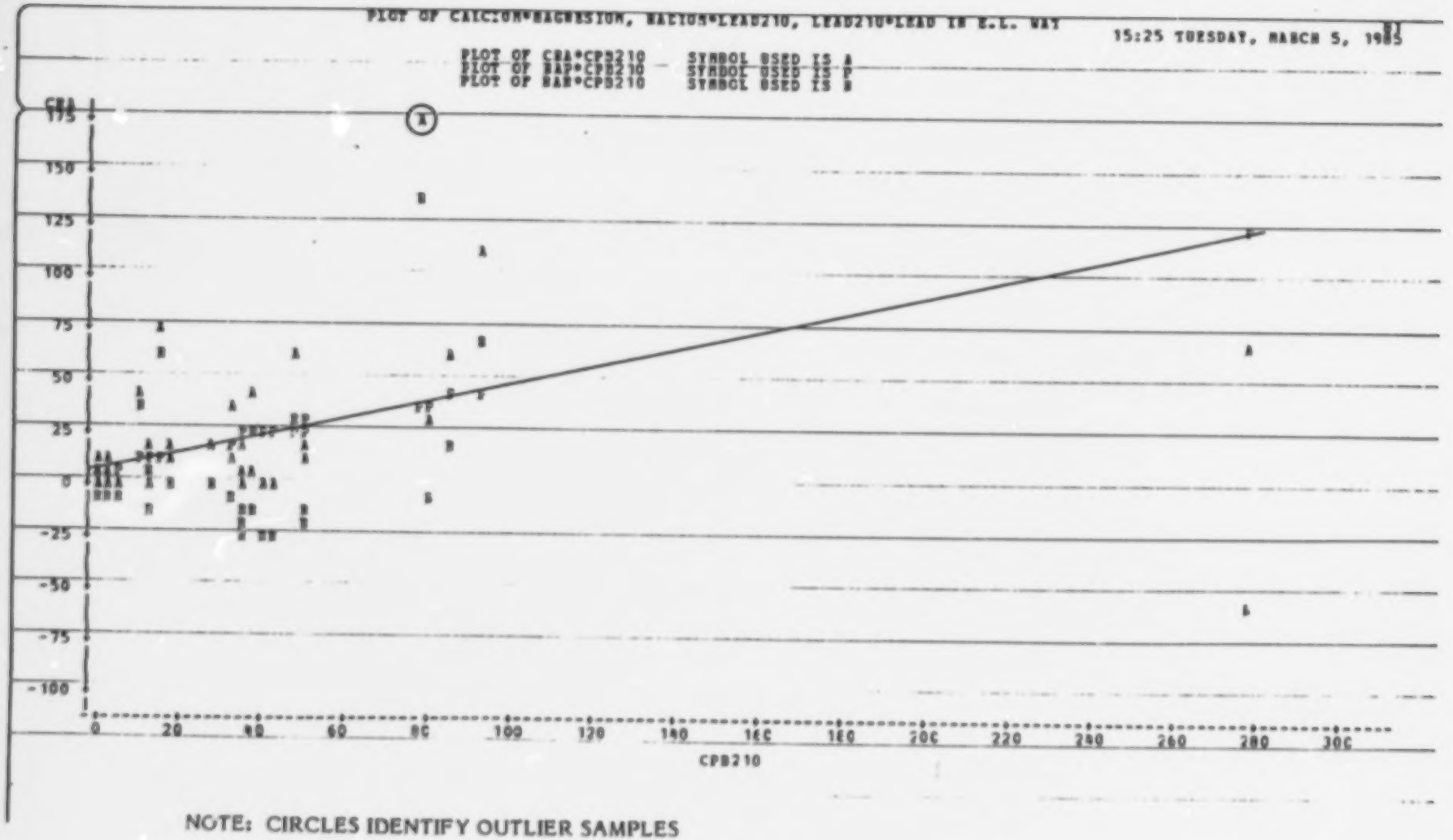
NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.6: RADIUM-226 VS. LEAD-210 IN BANCROFT VEGETATION



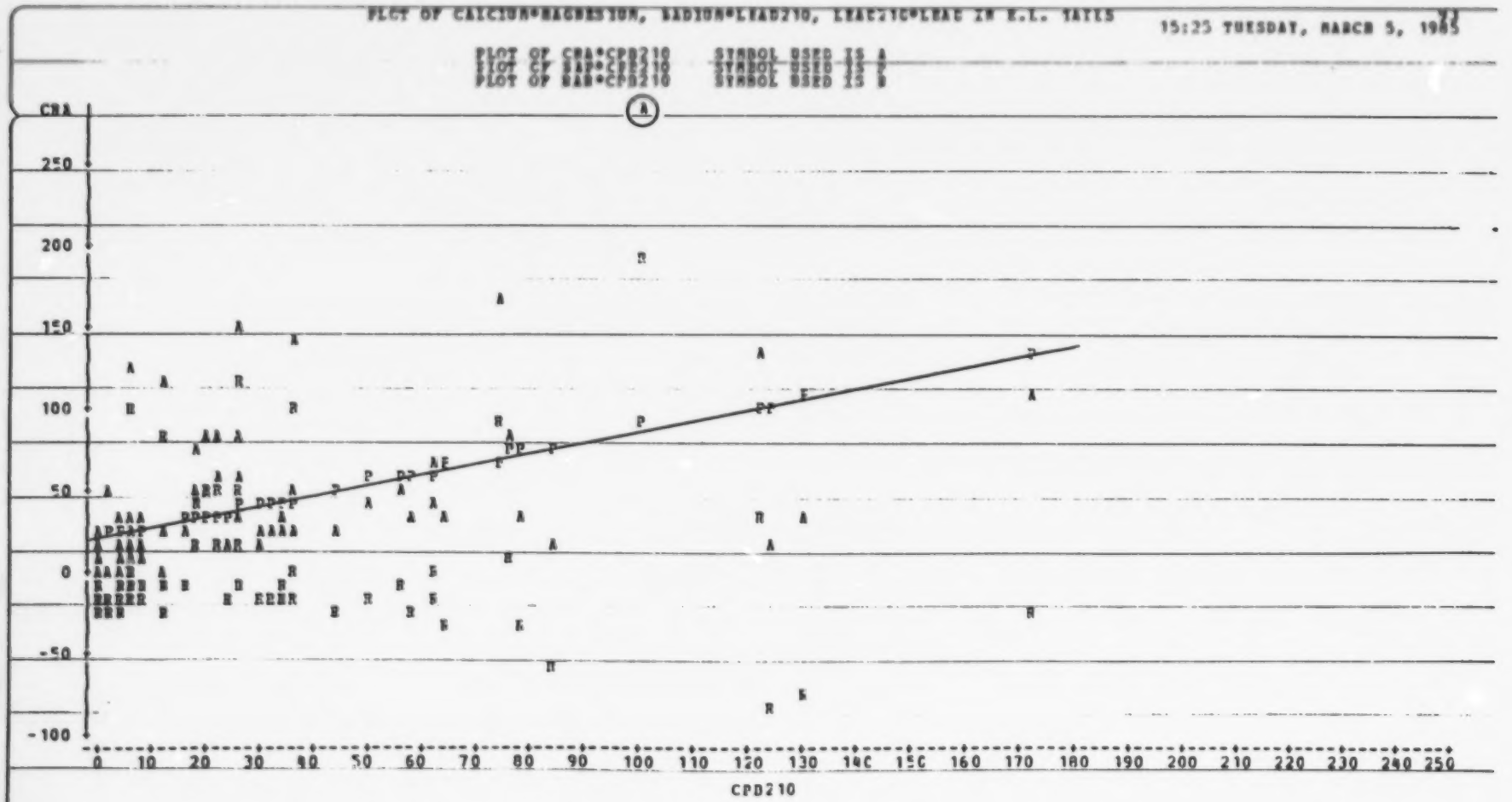
NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.7: RADIUM-226 VS. LEAD-210 IN ELLIOT LAKE WATER



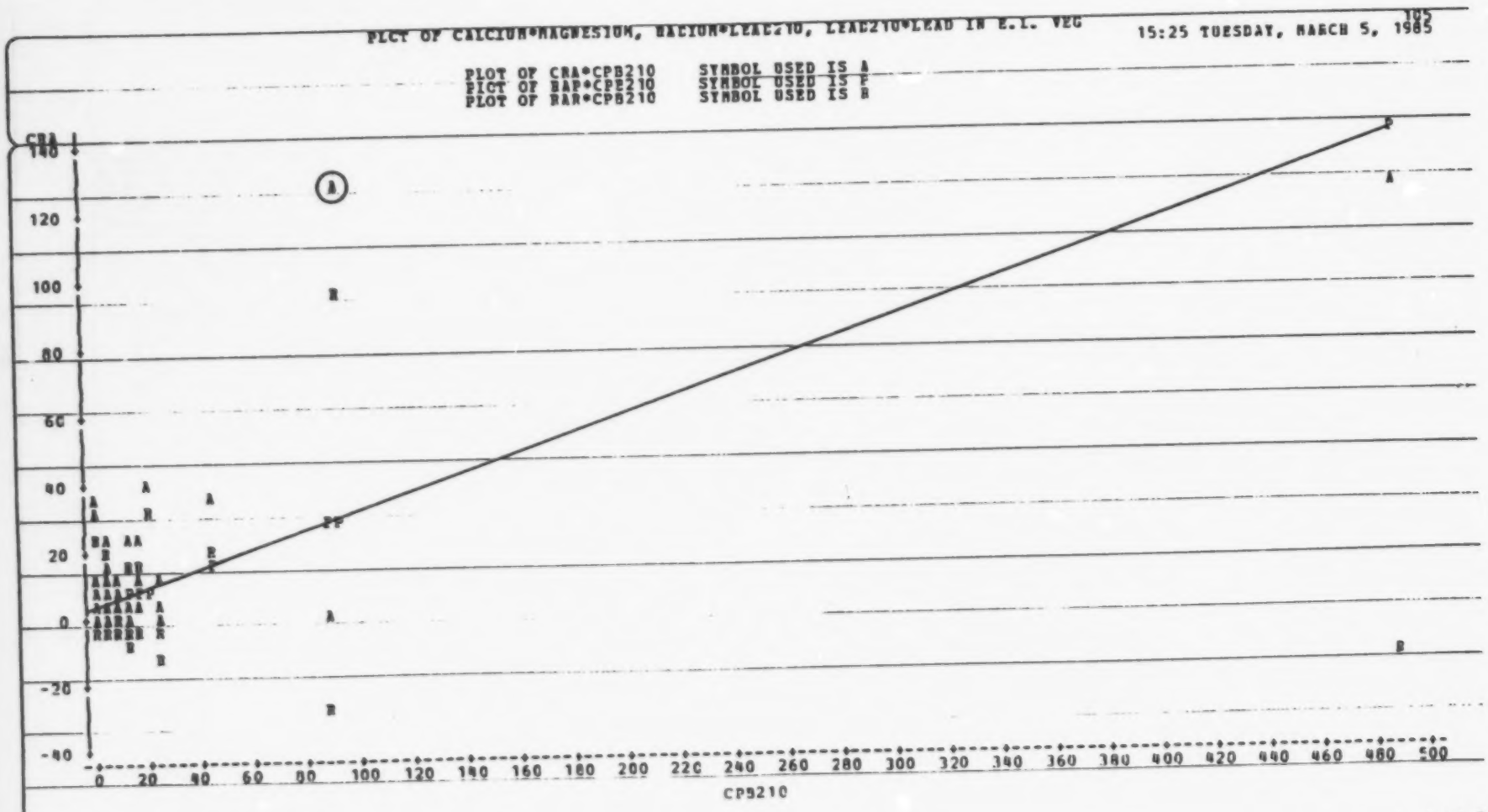
NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.8: RADIUM-226 VS. LEAD-210 IN ELLIOT LAKE TAILINGS


PLOT OF CALCIUM*REGRESSION, RADIUM*LEAD210, LEAC21C*LEAC ZN E.L. TAILS
15:25 TUESDAY, MARCH 5, 1985
PLOT OF CRA*CPB210 SYMBOL USED IS A
PLOT OF RAP*CPB210 SYMBOL USED IS P
PLOT OF RAB*CPB210 SYMBOL USED IS B
CRA
250
200
150
100
50
0
-50
-100
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250
CPB210

NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.9: RADIUM-226 VS. LEAD-210 IN ELLIOT LAKE VEGETATION


PLOT OF CALCIUM*MAGNESIUM, RADIUM*LEAD210, LEAD210*LEAD IN E.L. VEG
15:25 TUESDAY, MARCH 5, 1985
PLOT OF CRA*CPB210 SYMBOL USED IS A
PLOT OF RAP*CPB210 SYMBOL USED IS P
PLOT OF RAR*CPB210 SYMBOL USED IS R
CRA
140
120
100
80
60
40
20
0
-20
-40
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500
CPB210

NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.10: RADIUM-226 VS. LEAD-210 IN URANIUM CITY WATER

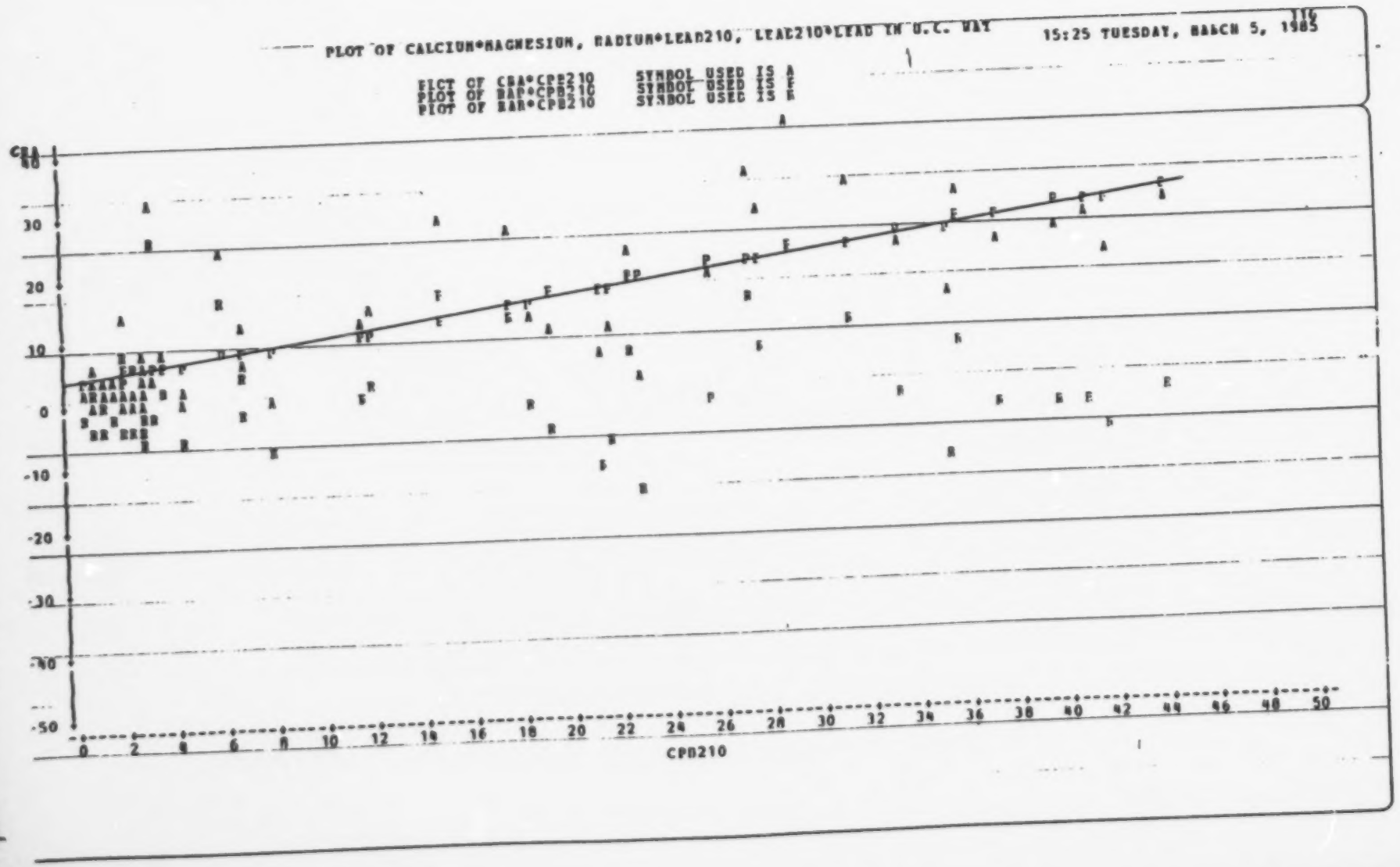
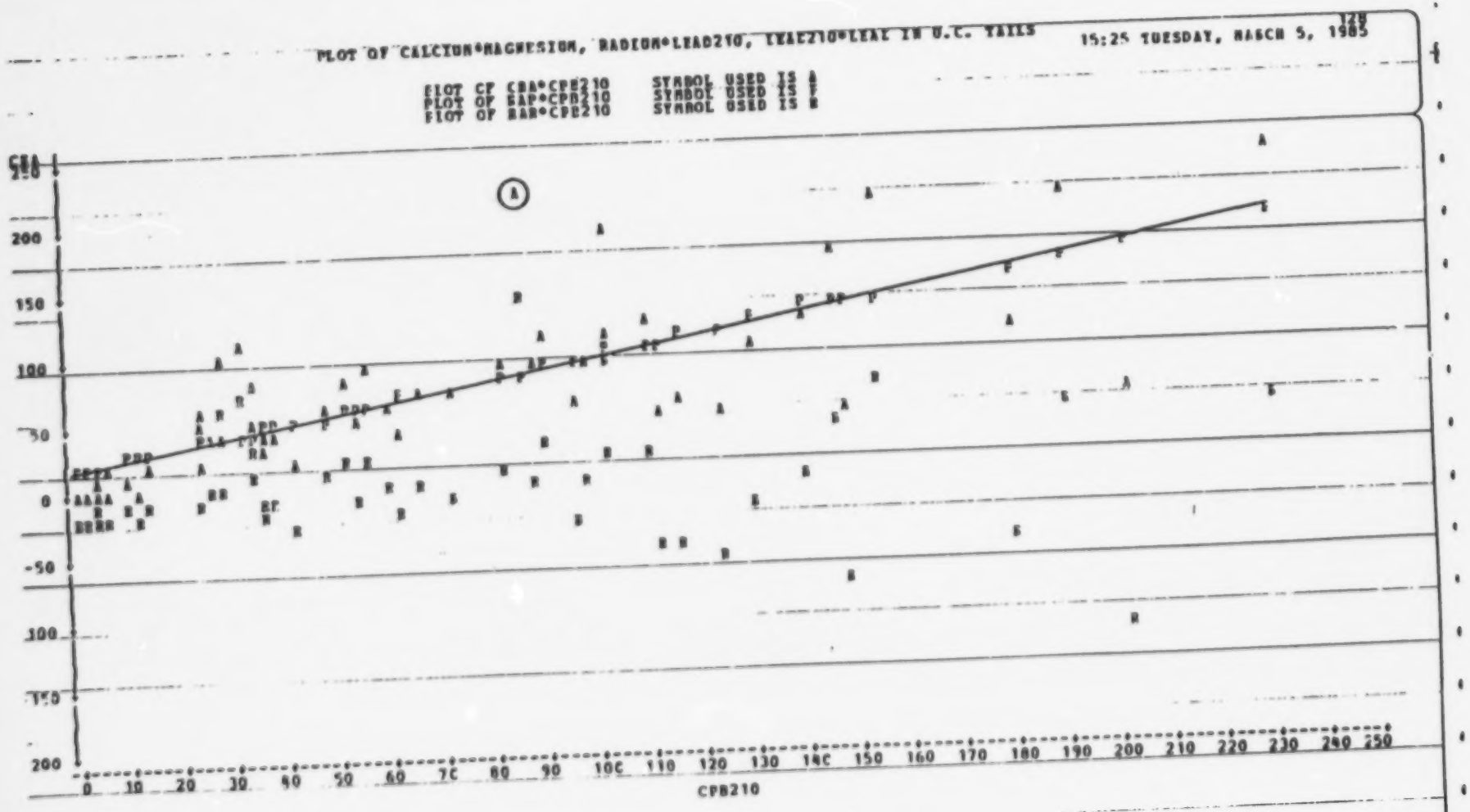
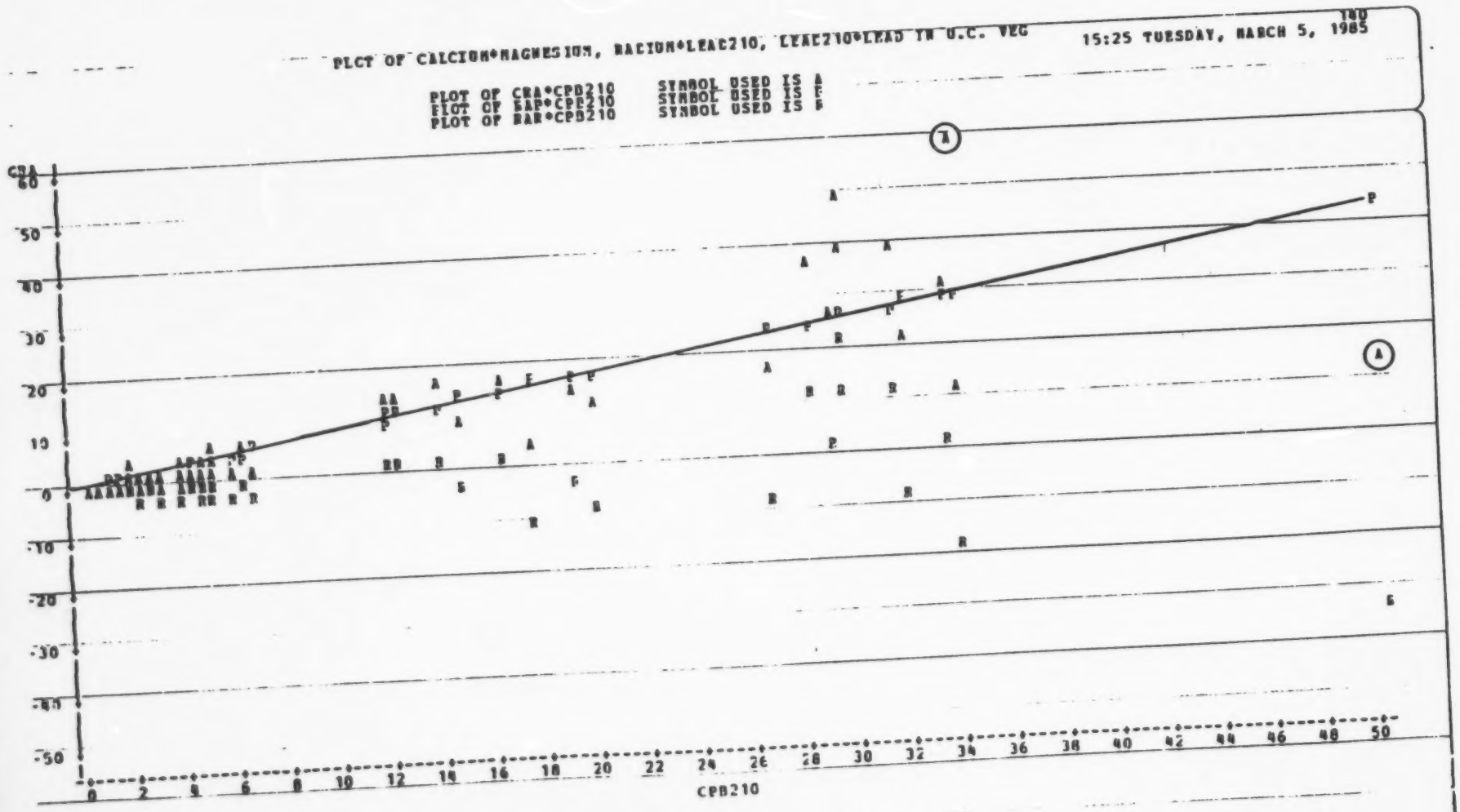

PLOT OF CALCIUM*MAGNESIUM, RADIUM*LEAD210, LEAD210*LEAD IN U.C. WAT
15:25 TUESDAY, MARCH 5, 1985
PLOT OF CRA*CPB210 SYMBOL USED IS A
PLOT OF RAP*CPB210 SYMBOL USED IS P
PLOT OF RAA*CPB210 SYMBOL USED IS R
CRA
60
30
20
10
0
-10
-20
-30
-40
-50
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50
CPB210

FIGURE A21.11: RADIUM-226 VS. LEAD-210 IN URANIUM CITY TAILINGS


PLOT OF CALCIUM*MAGNESIUM, RADIUM*LEAD210, LEAD210*LEAD IN U.C. TAILS
15:25 TUESDAY, MARCH 5, 1985
PLOT OF CRA*CPB210 SYMBOL USED IS A
PLOT OF RAP*CPB210 SYMBOL USED IS P
PLOT OF RAB*CPB210 SYMBOL USED IS B
CRA
250
200
150
100
50
0
-50
100
150
200
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250
CPB210

NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A21.12: RADIUM-226 VS. LEAD-210 IN URANIUM CITY VEGETATION



NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A22.1: CALCIUM VS. MAGNESIUM IN CONTROL WATER

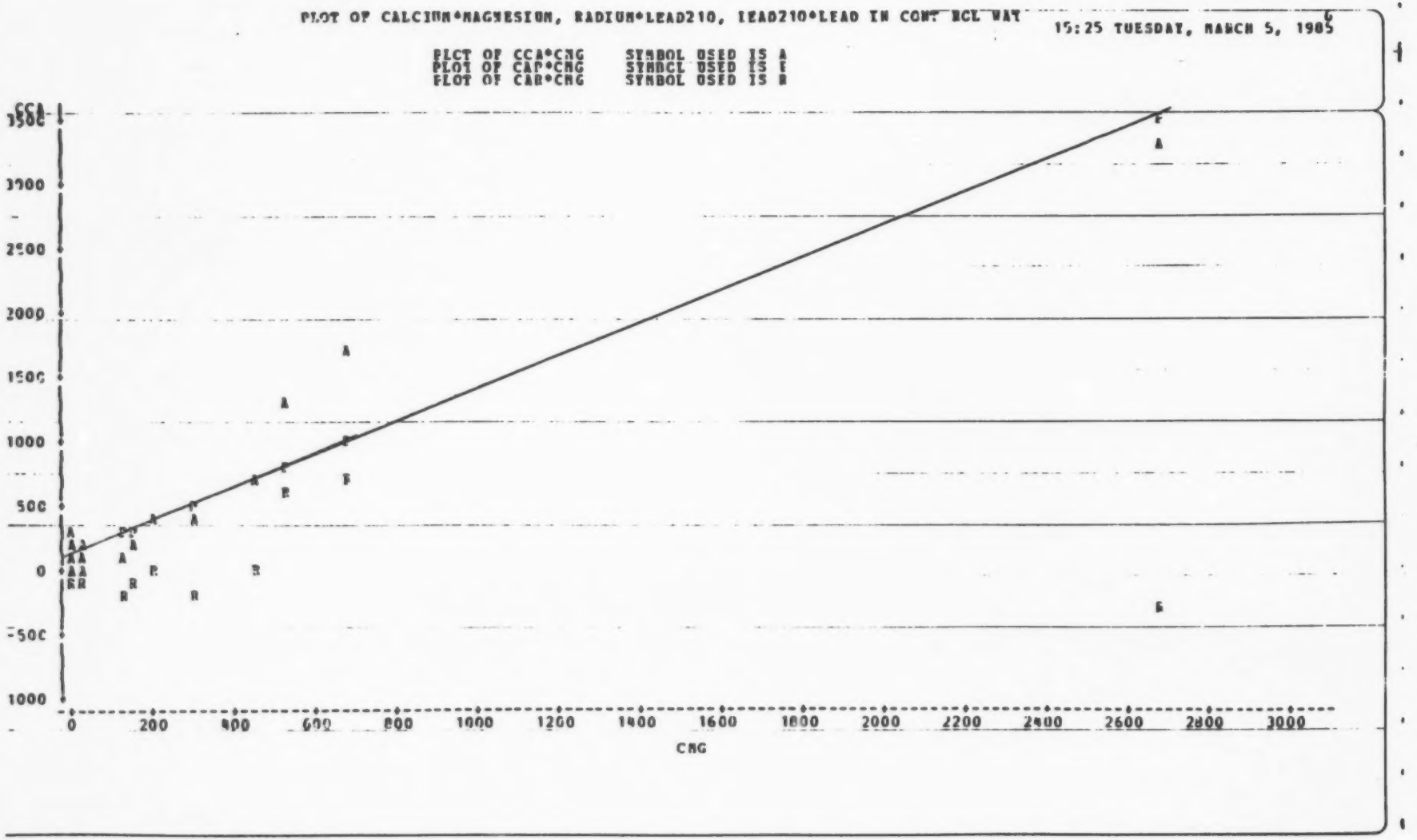


FIGURE A22.2: CALCIUM VS. MAGNESIUM IN CONTROL VEGETATION

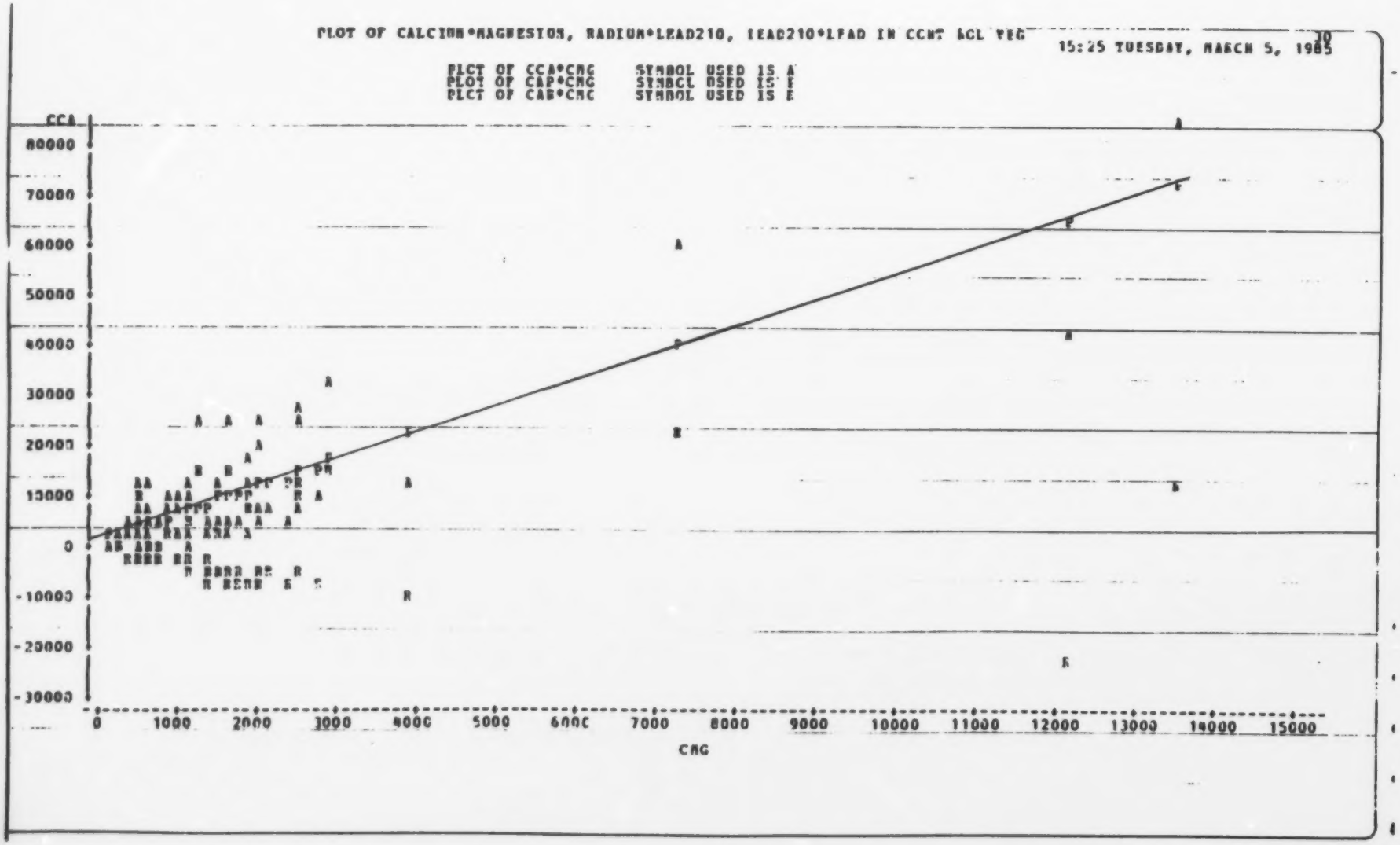


FIGURE A22.3: CALCIUM VS. MAGNESIUM IN BANCROFT WATER

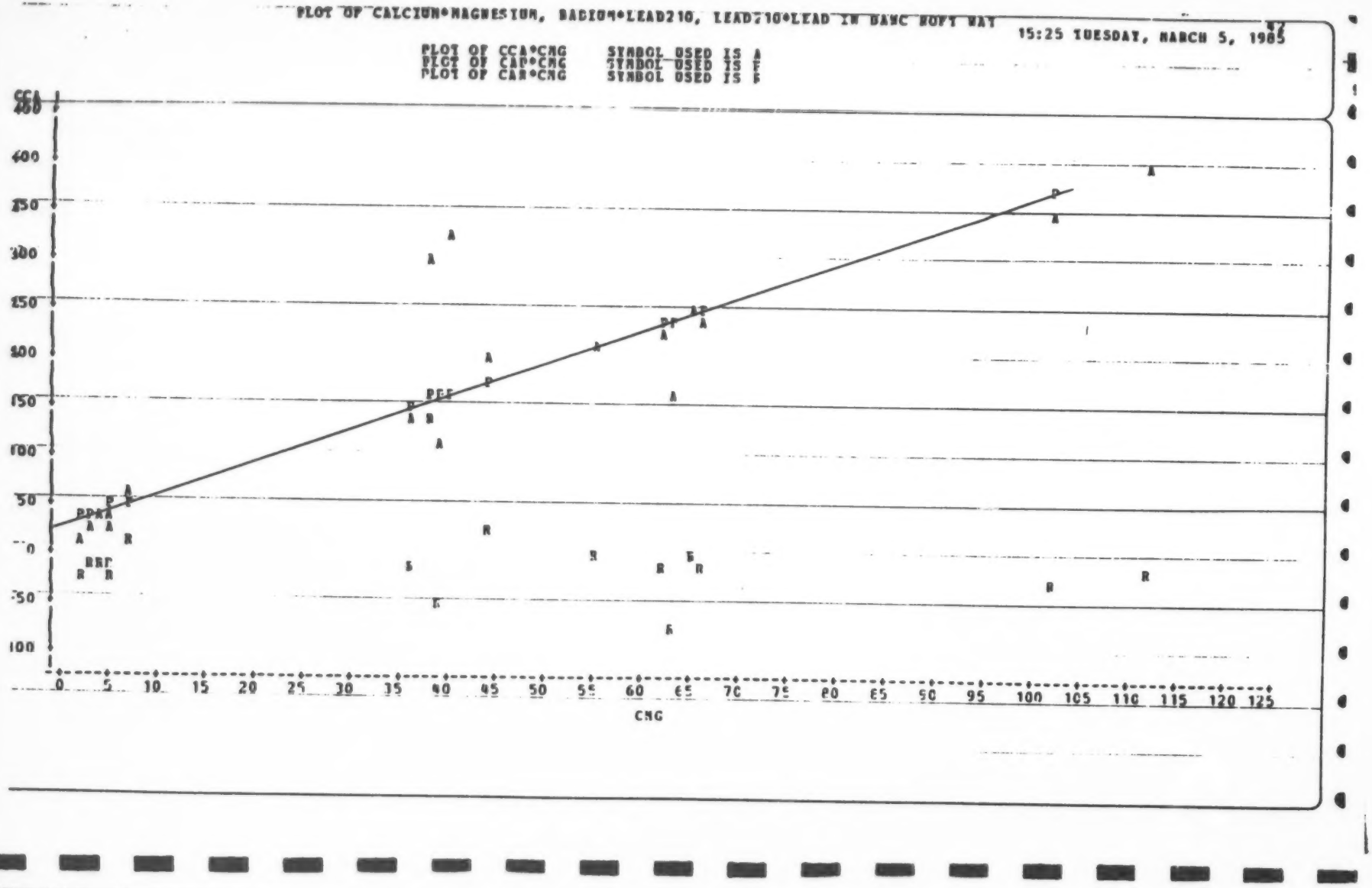
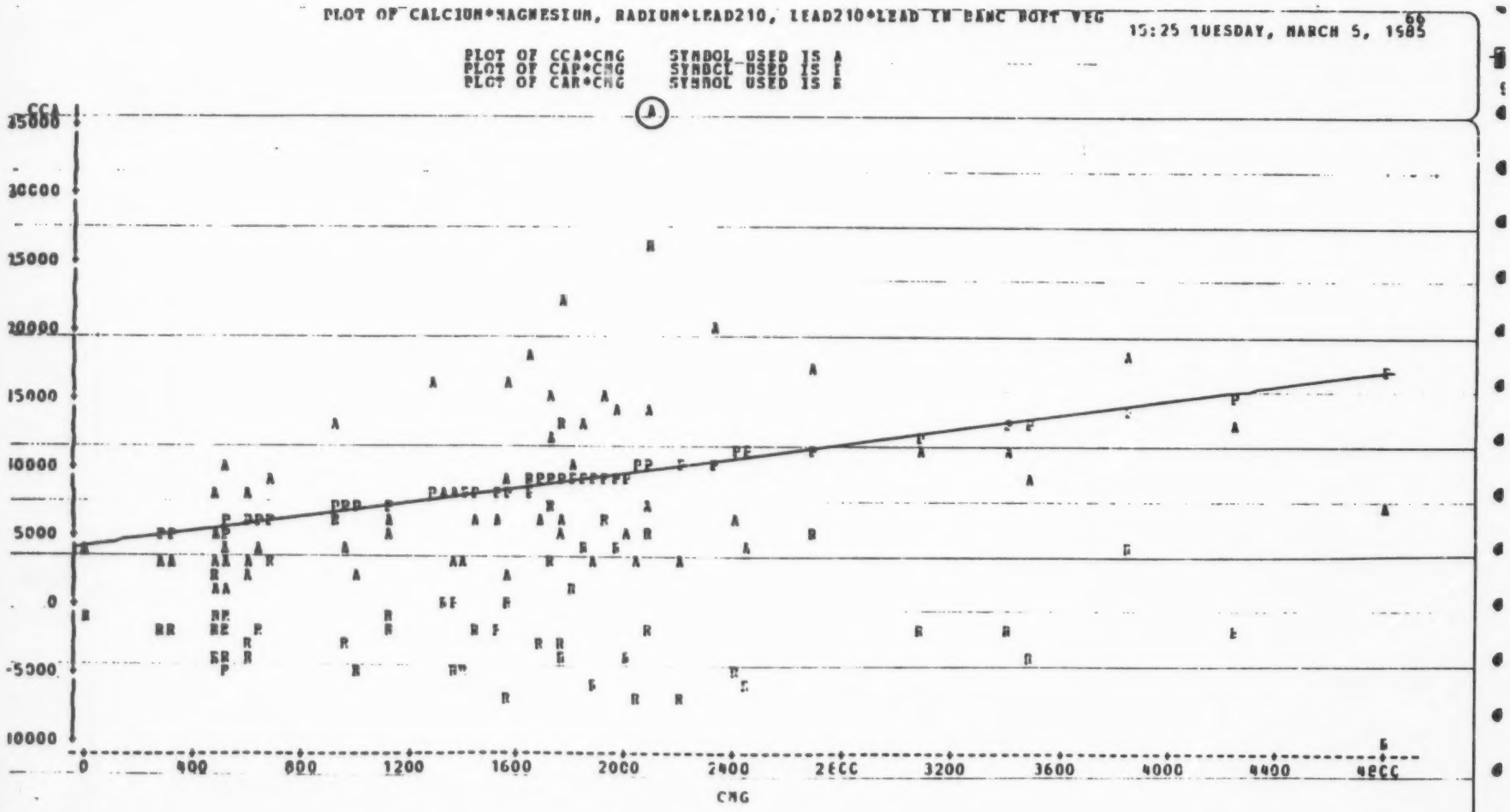
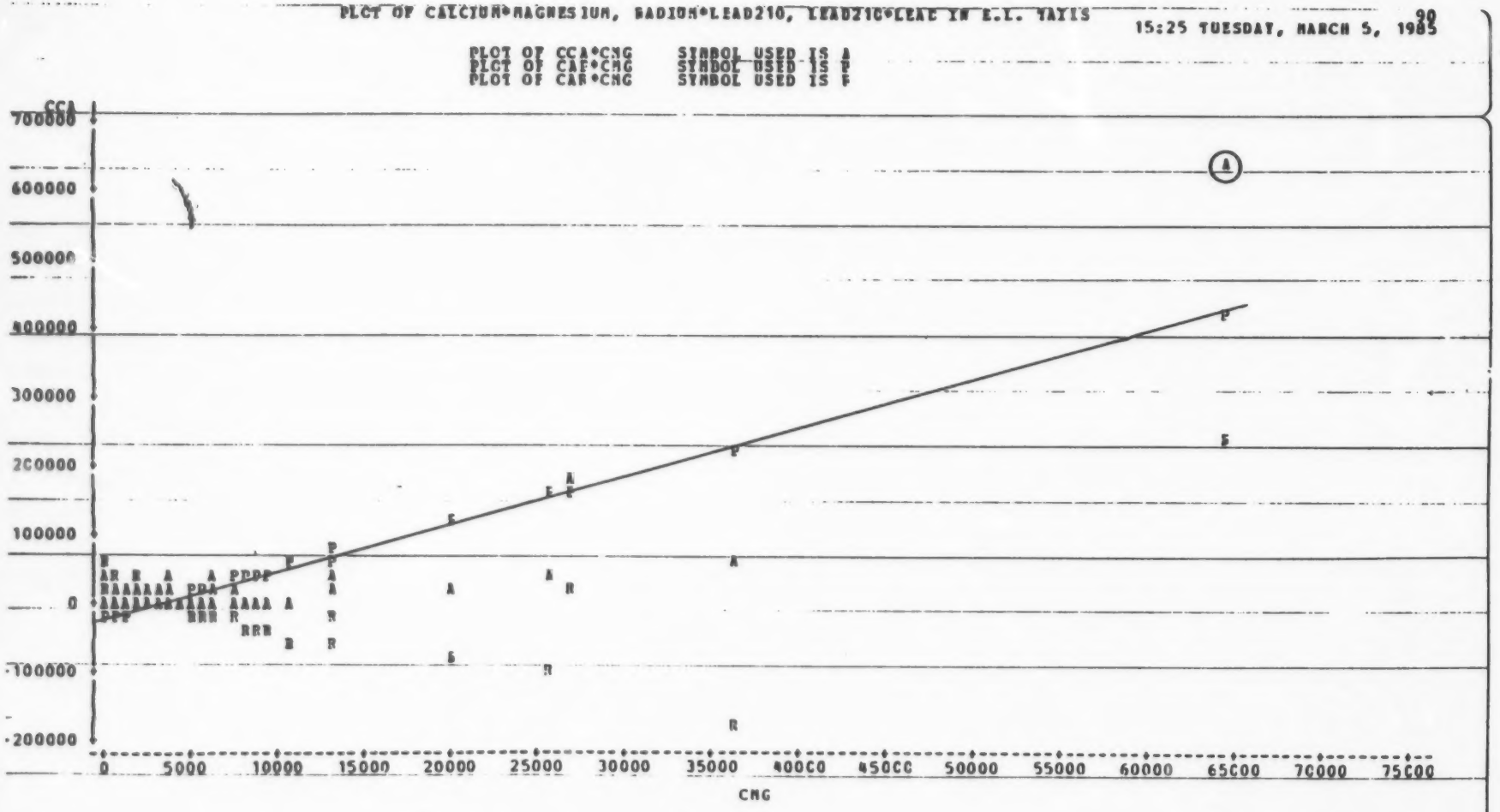

PLOT OF CALCIUM*MAGNESIUM, RADIUM*LEAD210, LEAD210*LEAD IN BANC HOPE WAY
15:25 TUESDAY, MARCH 5, 1985
PLOT OF CCA*CMG SYMBOL USED IS A
PLOT OF CAP*CMG SYMBOL USED IS P
PLOT OF CAR*CMG SYMBOL USED IS R
CCA
CMG

FIGURE A22.4: CALCIUM VS. MAGNESIUM IN BANCROFT VEGETATION



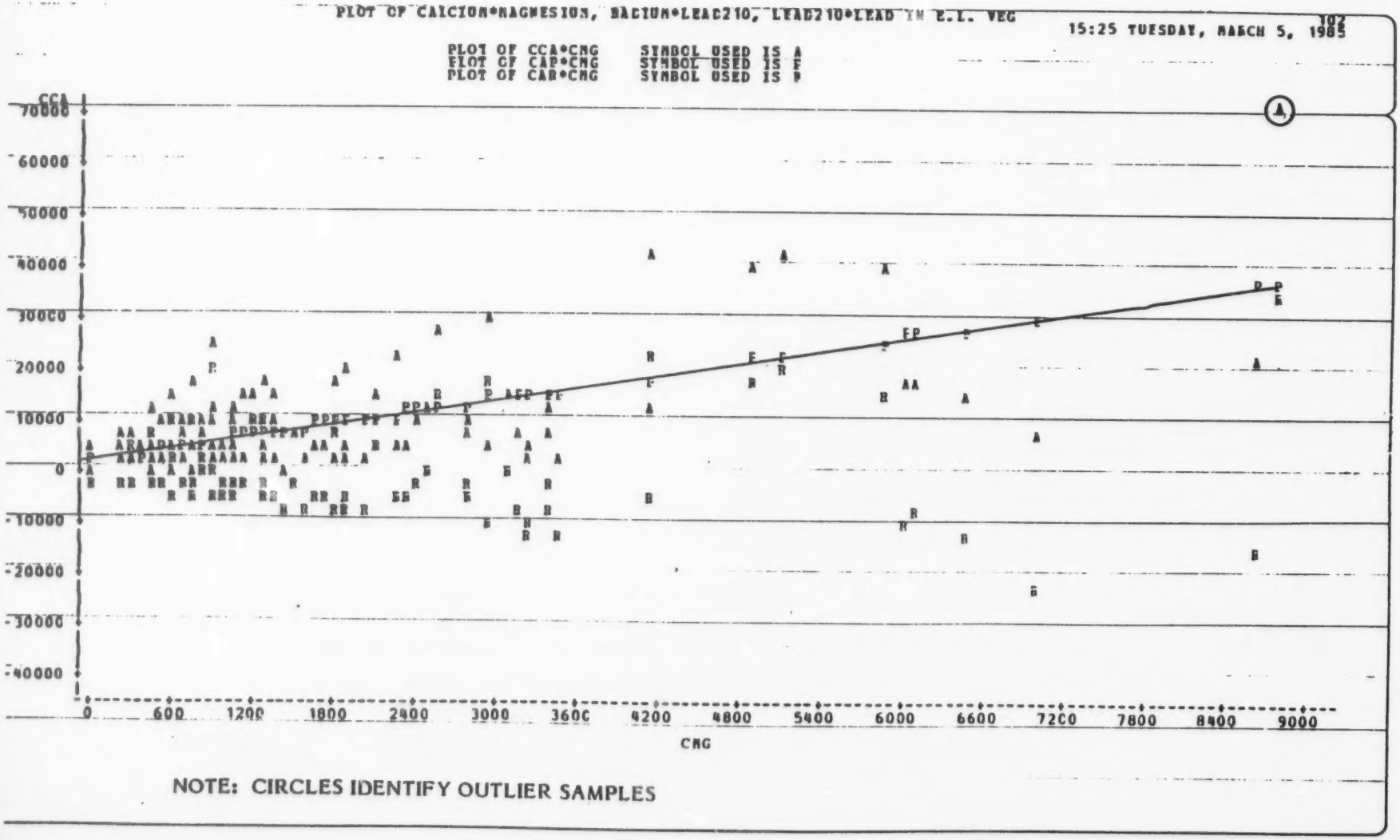
NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A22.5: CALCIUM VS. MAGNESIUM IN ELLIOT LAKE TAILINGS



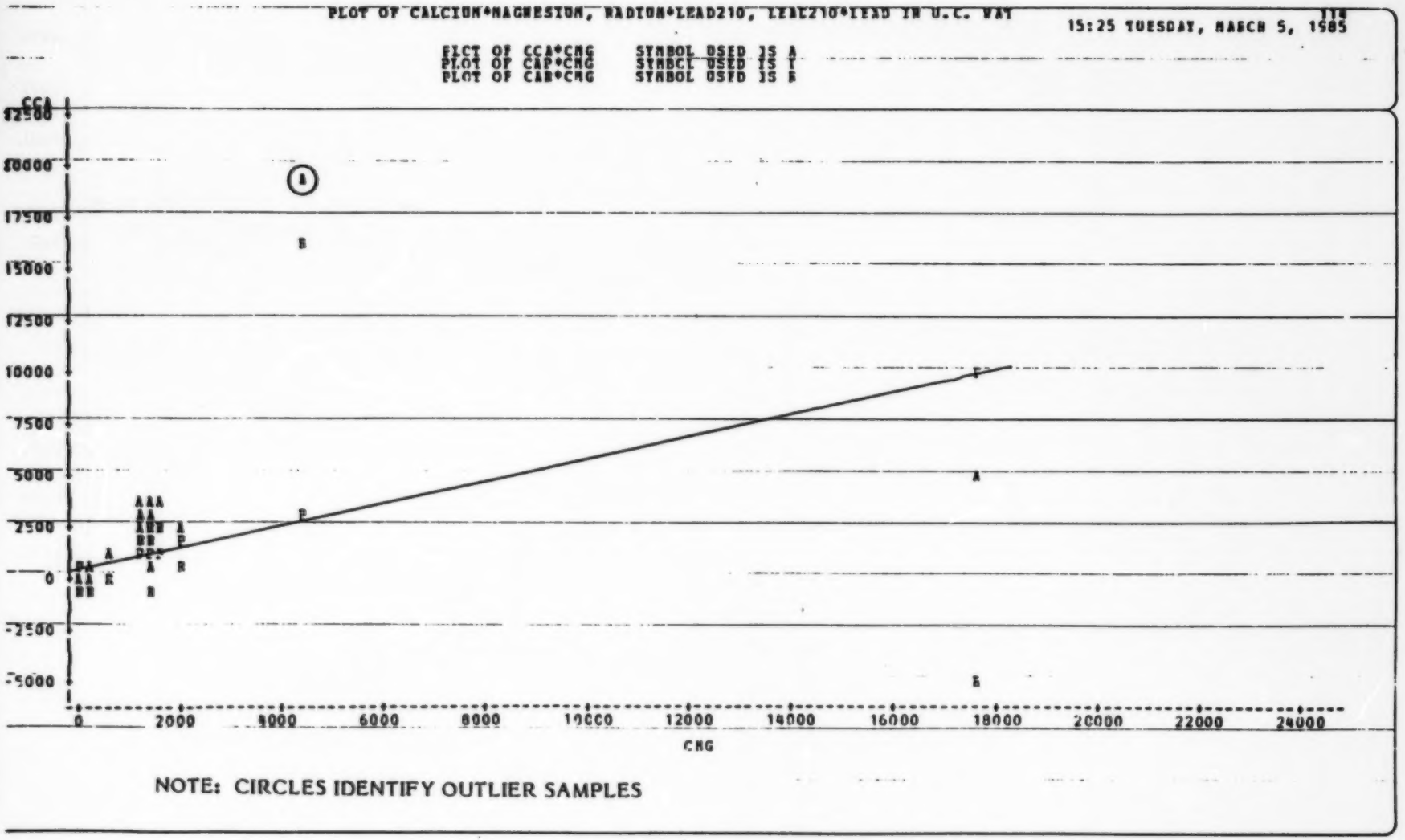
NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A22.6: CALCIUM VS. MAGNESIUM IN ELLIOT LAKE VEGETATION



NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A22.7: CALCIUM VS. MAGNESIUM IN URANIUM CITY WATER



NOTE: CIRCLES IDENTIFY OUTLIER SAMPLES

FIGURE A22.8: CALCIUM VS. MAGNESIUM IN URANIUM CITY TAILINGS

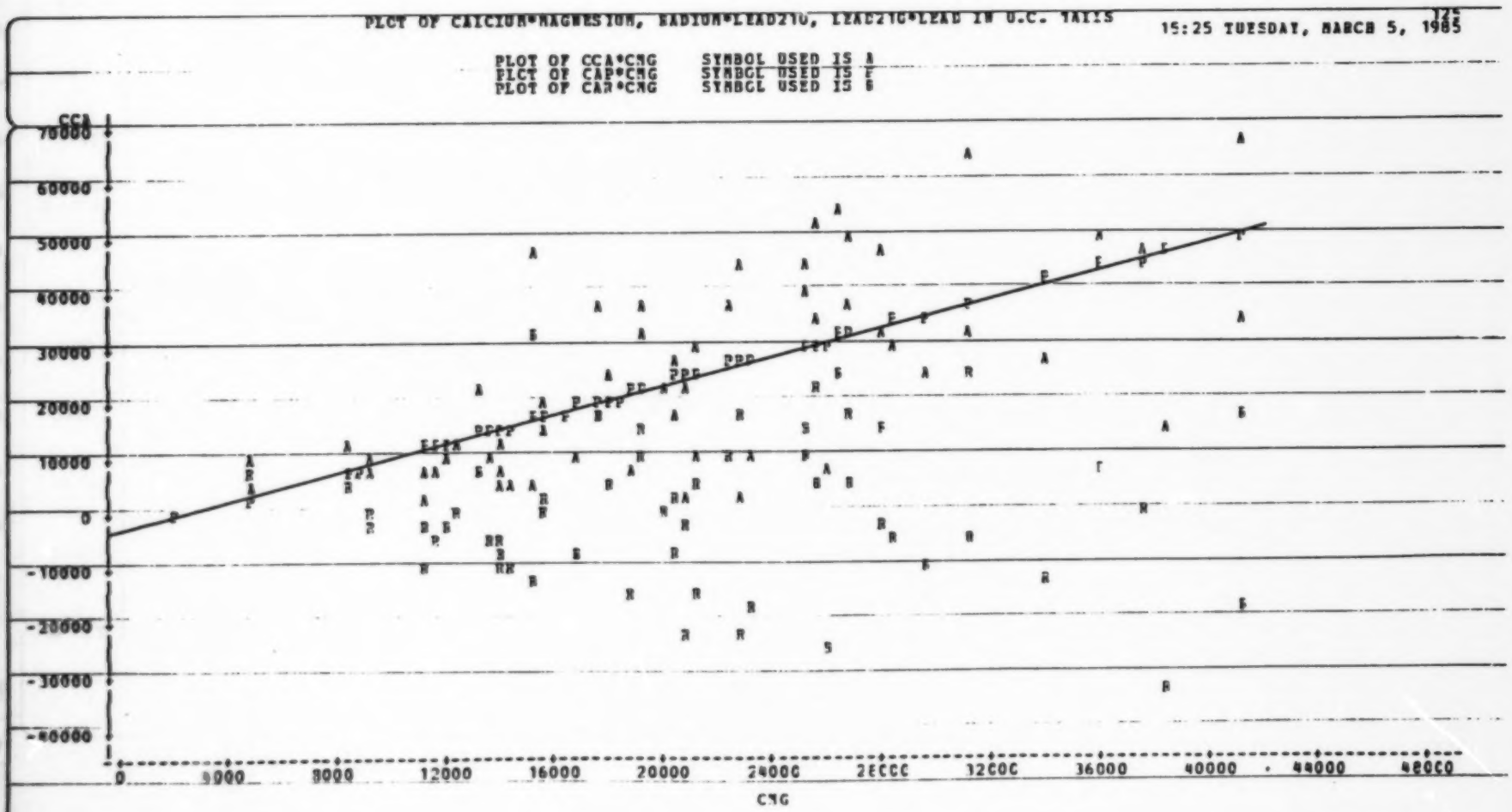


FIGURE A22.9: CALCIUM VS. MAGNESIUM IN URANIUM CITY VEGETATION

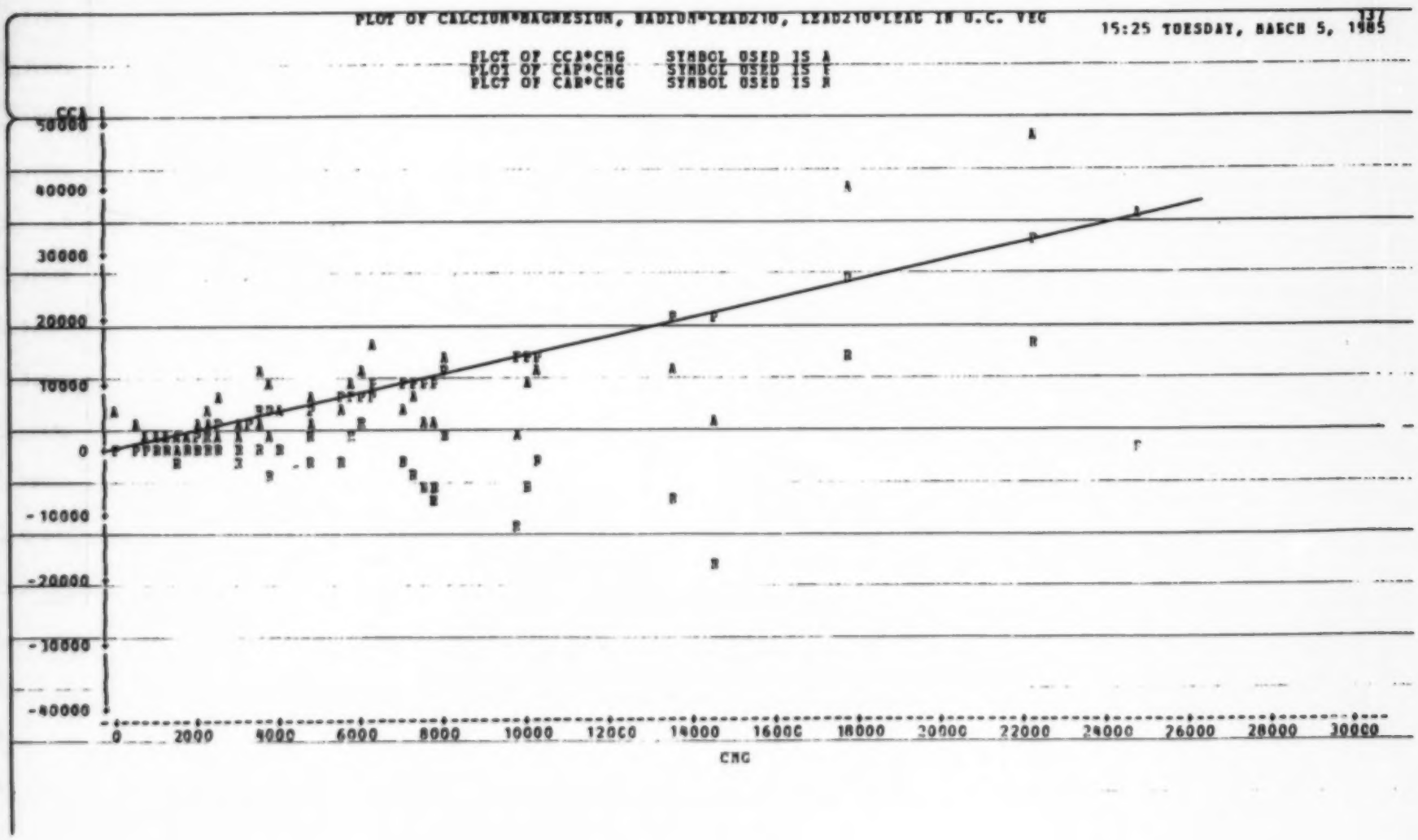


FIGURE A23: MERCURY VS. CLAY RESIDUAL DISTRIBUTION IN NIAGARA BASIN SEDIMENTS

Casewise Plot of Standardized Residual

Outliers = 3. *: Selected M: Missing

Case #	STN	-6. 0:.....: -3. :.....: 3. :.....:0 6.	HG	*PRED	*RESID
28	28.00	. * .. .	.44	4.7411	-4.3011
74	74.00	. ..* .	7.60	3.7191	3.8809

2 Outliers found.

Durbin-Watson Test = 1.07722

* *

Histogram - Standardized Residual

```
NExp N      (* = 2 Cases,    . : = Normal Curve)
1  .22   Out *
0  .43  3.00
3 1.10  2.67 :*
6 2.51  2.33 :**
7 5.13  2.00 **:*
* 9.39  1.67 ****:
* 15.4  1.33 *******:***
9 22.7  1.00 *****     .
* 29.8   .67 *********     .
* 35.2   .33 *********         .
* 37.2  0.0  ******************.
* 35.2  -.33 ******************:*****
* 29.8  -.67 **************:**********************
* 22.7 -1.00 ********* .
8 15.4 -1.33 ****    .
3 9.39 -1.67 **   .
2 5.13 -2.00 * .
1 2.51 -2.33 :
0 1.10 -2.67 .
0  .43 -3.00
1  .22   Out *
```

* *

Analysis of Variance

	DF	Sum of Squares	Mean Square
Regression	1	639.64751	639.64751
Residual	279	384.34069	1.37757

F = 464.33193 Signif F = .0000

FIGURE A24: MERCURY VS. ORGANIC CARBON RESIDUAL DISTRIBUTION IN NIAGARA BASIN SEDIMENTS

Casewise Plot of Standardized Residual

Outliers = 3. *: Selected M: Missing

Case #	STN	-6. 0:.....: -3.	3. :.....:0 6.	HG	*PRED	*RESID
28	28.00	. * ..	.	.44	4.3132	-3.8732
42	42.00	. ..*	.	7.24	4.4116	2.8284
68	68.00	. ..*	.	6.92	4.2342	2.6858
69	69.00	. ..*	.	6.92	4.0290	2.8910
74	74.00	. .. *	.	7.60	3.9388	3.6612

5 Outliers found.

Durbin-Watson Test = 1.41761

* *

Residuals Statistics:

Histogram - Standardized Residual

```
NExp N      (* = 1 Cases,    . : = Normal Curve)
3  .22   Out ***
1  .43  3.00 *
1 1.10  2.67 :
2 2.51  2.33 **.
3 5.13  2.00 *** .
* 9.39  1.67 ********:*
8 15.4  1.33 ********      .
* 22.7  1.00 ******************     .
* 29.8   .67 ************************      .
* 35.2   .33 ************************************:*
* 37.2  0.0  ************************************:********************
* 35.2  -.33 ************************************:****
* 29.8  -.67 ****************************** .
* 22.7 -1.00 ***********************:
* 15.4 -1.33 ************  .
* 9.39 -1.67 ********:***
1 5.13 -2.00 *   .
0 2.51 -2.33    .
1 1.10 -2.67 :
0  .43 -3.00
1  .22   Out *
```

Analysis of Variance

	DF	Sum of Squares	Mean Square
Regression	1	811.01285	811.01285
Residual	279	212.97535	.76335

F = 1062.43556 Signif F = .0000

FIGURE A25: CLAY VS. PARTICLE SIZE RESIDUAL DISTRIBUTION IN NIAGARA BASIN SEDIMENTS

Casewise Plot of Standardized Residual

Outliers = 3. *: Selected M: Missing

Case #	STN	-6. 0	-3.	3.	6. 0	CLAY	*PRED	*RESID
272	272.00	.	..*		.	0.0	-24.6468	24.6468
278	278.00	.	..*		.	0.0	-24.6468	24.6468
279	279.00	.	..*		.	0.0	-24.6468	24.6468
281	281.00	.	..*		.	0.0	-24.6468	24.6468

4 Outliers found.

Durbin-Watson Test = .97041

* *

Residuals Statistics:

Histogram - Standardized Residual

```
NExp N      (* = 1 Cases,    . : = Normal Curve)
4  .22   Out ****
0  .43  3.00
0 1.10  2.67 .
0 2.51  2.33   .
3 5.13  2.00 *** .
* 9.39  1.67 ********:**
* 15.4  1.33 ***************:
* 22.7  1.00 ************************:***
* 29.8   .67 ************************        .
* 35.2   .33 ************************              .
* 37.2  0.0  ************************************:************************
* 35.2  -.33 ************************************:
* 29.8  -.67 ********************************:*
* 22.7 -1.00 ***************          .
* 15.4 -1.33 ***************:***
6 9.39 -1.67 ******  .
9 5.13 -2.00 ****:****
3 2.51 -2.33 **:
0 1.10 -2.67 .
0  .43 -3.00
0  .22   Out
```

Analysis of Variance

	DF	Sum of Squares	Mean Square
Regression	1	135177.11126	135177.11126
Residual	279	15604.31468	55.92944

F = 2416.92217 Signif F = .0000

FIGURE A26: ZINC VS. ORGANIC CARBON RESIDUAL DISTRIBUTION IN NIAGARA BASIN SEDIMENTS

Casewise Plot of Standardized Residual

Outliers = 3. *: Selected M: Missing

Case #	STN	-6. 0:.....: -3. :.....: 3. :.....:0 6.	ZN	*PRED	*RESID
160	160.00	* .. .	93.30	338.3169	-245.0169
161	161.00	. * .. .	78.40	239.3022	-160.9022

2 Outliers found.

Durbin-Watson Test = 1.26963

* *

Histogram - Standardized Residual

```
NExp N      (* = 1 Cases,    . : = Normal Curve)
0  .22   Out
0  .43  3.00
1 1.10  2.67 :
1 2.51  2.33 * .
0 5.13  2.00     .
2 9.39  1.67 **      .
9 15.4  1.33 *********     .
* 22.7  1.00 **********************:*
* 29.8   .67 ******************************:**********************
* 35.2   .33 ************************************:*********************************
* 37.2  0.0  ***********************************   .
* 35.2  -.33 ***********************************   .
* 29.8  -.67 ***************                     .
* 22.7 -1.00 *************          .
7 15.4 -1.33 *******       .
7 9.39 -1.67 ******* .
5 5.13 -2.00 ****:
5 2.51 -2.33 **:**
3 1.10 -2.67 :**
2  .43 -3.00 **
2  .22   Out **
```

* *

Analysis of Variance

	DF	Sum of Squares	Mean Square
Regression	1	4854956.17043	4854956.17043
Residual	279	443219.07455	1588.59883

F = 3056.12472 Signif F = .0000

FIGURE A27: ORGANIC CARBON VS. P_2O_5 RESIDUAL DISTRIBUTION IN NIAGARA BASIN SEDIMENTS

Casewise Plot of Standardized Residual

Outliers = 3. *: Selected M: Missing

Case #	STN	-6. -3. 3. 6.	OCARB	*PRED	*RESID
11	11.00	. .. * .	4.33	2.8882	1.4368
152	152.00	. *.. .	1.00	2.2163	-1.2123
280	280.00	. * .. .	.13	1.4101	-1.2851

3 Outliers found.

Durbin-Watson Test = 1.70118

* *

Histogram - Standardized Residual

```
NExp N      (* = 1 Cases,     . : = Normal Curve)
1  .22   Out *
0  .43  3.00
1 1.10  2.67 :
1 2.51  2.33 * .
* 5.13  2.00 ****:*******
* 9.39  1.67 ********:*
* 15.4  1.33 ***********   .
* 22.7  1.00 ***************       .
* 29.8   .67 **************                .
* 35.2   .33 ************************************:**********
* 37.2  0.0  ************************************:***********
* 35.2  -.33 ************************************:***********
* 29.8  -.67 ******************************:***
* 22.7 -1.00 ***************       .
* 15.4 -1.33 ************  .
8 9.39 -1.67 ********.
5 5.13 -2.00 ****:
2 2.51 -2.33 **.
0 1.10 -2.67 .
0  .43 -3.00
2  .22   Out **
```

Analysis of Variance

	DF	Sum of Squares	Mean Square
Regression	1	383.00821	383.00821
Residual	279	38.87162	.13932

F = 2749.03138 Signif F = .0000